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SURVEY OF SEPARATION PROCESSES*

Third Progress Report on Problem No. 285-ML-55-4; File Serial 34

R. E. Clark

August 1, 1944

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SURVEY OF SEPARATION PROCESSES

SUMMARY

The purpose of this report in general is to provide information on the separation processes in which plutonium is separated from uranium and radioactive fission products and finally obtained as a concentrated product of high purity. Specifically this report describes the various separation processes which have been developed and gives their status as of June 1, 1944.

The chemical precipitation processes constitute the most important group of separation processes upon which development work has been done. The bismuth phosphate-lanthanum fluoride process is in operation at Clinton and will be operated at Hanford. Other processes in this group include lanthanum fluoride, sodium uranyl acetate, uranous oxalate, and columbic oxide. The Hanford process, of course, is the most important and has been studied the most extensively.

Other types of separation processes that have been investigated are resin adsorption, solvent extraction, and fractional volatilization. Considerable laboratory research work has been done on synthetic resin adsorption processes, some of the mechanical operations have been proved in the semi-works, and a design for use in the extraction step of the Clinton plant has been completed. Semi-works runs have been made on a continuous countercurrent ether extraction cycle. The fluorination step of the fractional volatilization or dry fluoride process has been performed in the semi-works. None of these methods has been established as a complete separation process for the extraction, decontamination, concentration, and isolation of plutonium.

On the basis of this survey it is concluded that none of the separation processes other than the present Hanford process and possibly the lanthanum fluoride process has been developed sufficiently for plant design and operation. It is believed that this report will be of value to those who are interested in securing a general knowledge of the separation processes, together with the current status of each. For this purpose it should be kept up to date. It is recommended that all process developments be evaluated in order to facilitate research. To expedite this evaluation it is suggested that each process be evaluated monthly by the research group responsible for its development and that this information be transmitted to an independent group for an overall evaluation of the developments in connection with all of the separation processes.

INTRODUCTION

The objective of this program is to follow all developments on the separations processes, to maintain an index of the sources of detailed information, and to condense the more significant facts and data into summaries for the Technical Division, General Engineering files. Reports CN-1017 and CN-1603, which include descriptions, flowsheets and critical evaluations of the main line and four alternate separation processes, were prepared on this authorization and have been issued. These reports, however, cover only the period prior to October 1, 1943. The purpose of the present report is to summarize the development work on various separation processes up to June 1, 1944.

For the preparation of this report the project literature has been reviewed and the data included herein are primarily from this source. In order to provide a substantially complete record of this separation work, an attempt has been made to mention in this report all of the separation carriers even though several of these are of very minor importance and complete processes have not been developed for them. Since an endless number of process couplings is possible, only the more important ones have been described.

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GENERAL DISCUSSION

The purpose of the Hanford plant is to produce a plutonium compound in satisfactory yield and purity. The plutonium (Pu) is manufactured by a self-sustained nuclear chain reaction through the adsorption of slow or thermal neutrons by $_{92}U^{238}$. Fast neutrons are furnished through the fission of $_{92}U^{235}$ and are moderated to thermal energy by transmission through graphite. These reactions take place in a "pile" which consists of a large cubical structure of graphite blocks with horizontal Al tubes spaced throughout in a lattice arrangement. These tubes are filled with U cylinders or slugs (8 in. long by 1.36 in. dia.). Large quantities of cooling water are passed through the tubes to prevent damage to the pile from the heat of reaction. The slugs are enclosed in Al jackets 35 mils thick, which prevent corrosion of the U and attendant removal of the nuclear reaction products by the cooling water.

In operation of the Hanford plant it is planned to irradiate the slugs about 100 days at 250,000 KW power level. An average of 250 grams of Pu will be produced per ton of U when the pile contains 100 tons of U. In addition, approximately 279 grams of mixed fission products per ton of U will be formed simultaneously. Of this amount about 13 grams are radioactive after 60 days storage.

After 100 days operation the slugs are pushed from the pile and stored under water for 60 days. The purpose of this storage is twofold. During this period a considerable quantity of $_{93}Np^{239}$ changes to Pu. Also the gamma activity associated with the average ton of U decreases from 10^8 to 10^5 curies. One of the purposes of the separation process is to reduce this activity to about 0.010 curies. This is the maximum amount of radioactivity with which a person can work routinely with some lead shielding and other precautions.

The distribution of fission products present following the 60-day storage or "cooling" period is shown in Table I. The amounts of major active fission isotopes are compared with the total amount of these elements present. It should be pointed out that not all of the fission products will be radioactive, because stable ends of the decay chains will be there also. Estimates are also given of the amounts of fission products present which have no significant radioactive portions after the cooling period is over (MUC-GTS-745).

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Table I

FISSION PRODUCT CONTENT OF PILE METAL
100 days operation at 2500 KW/ton, 60 days decay
(Ref. MUC-GTS-745)

Fission Products with Active Isotopes

Active Isotopes	Gm/ton U	Total Isotopes (active & inactive)	Gm/ton U
55d Sr	1.32	Sr	10.7
57d Y	1.3	Y	7.5
65d Zr*	1.35	Zr	26.5
35d Cb*	1.01	Cb	12.2
40d Ru*	0.84	Ru	14
330d Ru	0.45		
8d I	0.002	I	1.75
12.5d Ba	0.055	Ba	11
40h La*	0.0086	La	11
28d Ce	0.605	Ce	29.2
340d Ce	6.4		
17m Pr	0.00022	Pr	13
Total	13	Total	137

Fission Products with No Active Isotopes

	Gm/ton U		Gm/ton U
Se	0.25	Sb	0.05
Br	0.15	Te	3.25
Kr	3.75	Xe	29.8
Rb	4.5	Cs	29
Mo	21.7	Nd	28.2
43	7.25	Sm	8.25
Rh	2.5	Eu	1.25
Pd	1.5	Gd	0.05
Ag	0.225	Total	142

Total grams of active fission products per ton of U = 13
Total grams of inactive fission products per ton of U = 266
279

* Important gamma emitters

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After cooling, the slugs are transferred under water to the separations area for processing. The purpose of the separation process is to obtain a pure product decontaminated by a factor of 10^7 for gamma activity. Because of the high radiation levels these operations must be carried out by remote control and behind shielding. The separation procedure is complicated by two main factors: (1) the fission products constitute a mixture of elements with diverse chemical properties; (2) a variety of radioactive elements must be removed simultaneously to levels less than 1 p.p.m.

The four types of separation methods which have been developed are chemical precipitation, solvent extraction, adsorption, and fractional volatilization. The first three types are often referred to as the wet processes and the last one as a dry process. Various couplings of the different types of processes are possible and many of these have been tried.

The first separation step in the wet processes is the removal of the Al jacket and dissolution of the U. The aluminum-jacketed slugs are dumped from the storage baskets into a dissolver where the Al jacket is dissolved and the resulting solution jetted to waste. The U is then dissolved with HNO_3. In subsequent steps, which vary with the type of process, Pu is extracted from the U solution, the Pu solution is decontaminated and concentrated, and finally the Pu is isolated in a concentrated solution of high purity.

The precipitation processes for the separation of Pu consist of a succession of precipitations in which Pu and fission products are co-precipitated with inactive compounds, such as $BiPO_4$ and LaF_3. These inactive compounds, which are called "carriers", are selected so that Pu is co-precipitated or "carried" in only one of its oxidation states. The precipitation conditions are regulated so that a minimum amount of fission products is carried simultaneously with Pu and a substantial fraction is carried when Pu is not co-precipitated.

In the solvent extraction processes the Pu and a small percentage of fission products are extracted from an aqueous UN solution by an immiscible solvent and then the Pu is extracted from the solvent by a small volume of aqueous UN solution. This cycle can be repeated for additional decontamination, concentration and purification.

In the adsorption processes Pu together with some U and fission products is adsorbed in a resin-packed column. These elements are then elutriated from the column selectively. Subsequent cycles can be performed for additional decontamination, concentration and isolation.

In the fractional volatilization or so-called dry process, F_2 is passed over the slugs and volatile fluorides of U, Pu and a few fission products are formed, leaving behind most of the fission products. These volatile fluorides are condensed and then separated by distillation.

Various processes have been developed for the four types of separation methods mentioned above. These are described in detail in the following sections of this report, which includes their status as of June 1, 1944.

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JACKET REMOVAL AND METAL SOLUTION

Jacket removal and metal solution are the first steps in all the wet separation processes. Jacket removal or laceration is the first step in the dry process.

Jacket Removal

The U slugs are jacketed with Al which may or may not be bonded to the U. The purpose of the jackets is to prevent corrosion by cooling water in the pile and resulting contamination of this water by Pu and fission products. The advantages of using a bond are better heat transfer and also minimized undercutting of the Al jacket by water if corrosion through the jacket occurs. The different bonds that have been used include Zn, Zn-Sn, and Al-Si. The slugs are dipped into a melt of the bonding material, inserted into Al cans, and then Al caps are welded on. The Al-Si bond for the Al jackets has been used the most extensively, but it is the most difficult to remove.

The Al jackets must be removed in the separation process. In the wet processes the Al would interfere chemically in the extraction step. In the dry fluoride processes the jackets must either be dissolved off or lacerated to permit fluorination of the U slug inside. The principal jacket removal methods are shown in Table II. The Al can be dissolved in 10% HNO_3 plus 0.1% $Hg(NO_3)_2$, which acts as a catalyst. This solution will also remove Zn and Zn-Sn but not Al-Si bonds. The latter can be removed by an additional treatment with NaOH. It is planned to use Al-Si bonded slugs at Hanford and the above method using $HNO_3 + Hg(NO_3)_2$ followed by NaOH is tentatively specified on the Hanford flowsheet dated March 29, 1944. The methods involving HF and H_3PO_4 do not appear attractive. The HF forms a precipitate, possibly UF_4, which adheres to the U. The H_3PO_4 requires a high temperature (180-200°C.) and causes a high U loss. Both HF and H_3PO_4 would probably present corrosion problems. Recently favorable results have been obtained with $NaOH + NaNO_3$ followed by $HNO_3 + Hg(NO_3)_2$ to complete the scale removal.

The following equations typify the possible reactions for jacket removal:

$$Al + 4\ HNO_3 \longrightarrow Al(NO_3)_3 + NO + H_2O \qquad (1)$$

$$2\ Al + 2\ NaOH + 2\ H_2O \longrightarrow 2\ NaAlO_2 + 3\ H_2 \qquad (2)$$

$$Si + 2\ NaOH + H_2O \longrightarrow Na_2SiO_3 + 2\ H_2 \qquad (3)$$

$$8\ Al + 5\ NaOH + 3\ NaNO_3 + 2\ H_2O \longrightarrow 8\ NaAlO_2 + 3\ NH_3 \qquad (4)$$

As stated previously, the Al-Si bond is difficult to remove. It is believed that a ternary alloy (Al, Si, U) is formed between the bond and U. Because an Al-Si alloy itself will dissolve slowly in NaOH, the difficultly soluble scale which remains on the slug is believed to be this ternary alloy. Since no promising method has been developed for the removal of this scale completely by dissolution with NaOH, the approach has been to dissolve the Al jacket and the Al-Si alloy and then to remove the small amount of insoluble scale so as to produce a relatively clean slug. If the scale is then slurried from the dissolver prior to the dissolution of the U metal, the final metal solution should contain only small amounts of it. The amount of the scale removed appears to increase slightly with increasing NaOH concentrations up to about 30%. The amount of scale removed is not sufficiently increased, however, with solutions more concentrated than 30%. The maximum amount of H_2 evolution during the treatment is not greatly altered by variations of NaOH concentrations and appears to be about 200 c.f.m. per 6 ton charge of Hanford slugs. The addition of H_2O_2 to NaOH solutions improves the scale removal. The amount of H_2O_2 required decreases as the NaOH concentration increases. Thus with 30% NaOH, 10% of H_2O_2 added slowly over one hour was required to remove more than 90% of the scale from a 1-in. section of an Al-Si bonded slug. With 50% NaOH, however, only 4% of H_2O_2 added slowly over one-half hour was needed.

Laboratory studies of the rates of gas evolution and dissolution of Al have been made. The use of a NaOH-$NaNO_3$ solution reduced the H_2 evolution to less than 0.5% of that which was produced by the use of NaOH alone. The quantity of NH_3 produced when Al was dissolved in a NaOH-$NaNO_3$ solution was substantially equal to that indicated by Equation 4. The reduction of H_2 evolution is desirable to minimize the danger of an explosion. These experiments were performed using solutions at 70°C. in which the NaOH concentration was varied from 2 M to 5 M and the $NaNO_3$ concentration was varied from 1 M to 4 M. In the same range of concentrations the rate of dissolution of the Al was not significantly changed by variations in the concentrations of $NaNO_3$ and NaOH. However, an increase of the temperature from 60 - 100°C. tripled the rate of dissolution of the Al throughout the range of NaOH and $NaNO_3$ concentrations studied above. At 100°C. the H_2 evolution was still less than 2% of that which is obtained with NaOH alone under the same conditions. Preliminary experiments in which the Al-Si alloy was dissolved in NaOH-$NaNO_3$ solutions suggest that $NaNO_3$ does not reduce the evolution of H_2 in the reaction of Si with NaOH (Equation 3). At 100°C. the calculated maximum rate of NH_3 evolution per 6-ton U charge will be about 200 c.f.m. when the Al jacket is dissolved in NaOH-$NaNO_3$ solutions. Using HNO_3 + 0.06% $Hg(NO_3)_2$ solution for dissolving the Al jacket (Equation 1) the rate of dissolution of this jacket will be about in direct proportion to the HNO_3 concentration and the calculated rate of NO evolution at Hanford (6-ton charge) using 10% HNO_3 is 216 c.f.m. (N-1057).

Since it appears that the complete removal of the Al-Si bonded jacket will require prolonged treatments with either HNO_3 or NaOH the rate of dissolution of the U metal in these coating removal solutions was investigated. The rate of dissolution of U in NaOH solutions was found to increase slightly as the NaOH concentration increased. However, even in 50% NaOH the calculated weight loss for a clean Hanford slug was less than 0.2% per hour. On the other hand, increasing the HNO_3 concentration from 10 to 30% increased the calculated weight loss from 0.14 to 1.1% per hour. The presence of $Al(NO_3)_3$ in HNO_3 greatly increased the rate of dissolution, whereas the presence of either $NaNO_3$ or $NaAlO_2$ did not materially alter the rate of dissolution by NaOH.

[redacted]

Five runs on a semi-works scale testing the effects on the $BiPO_4$ separations process of the insoluble material remaining after the removal of the Al-Si bonded jacket have been completed. After jetting the jacket removal solutions from the dissolver, the insoluble scale carried with them was separated and returned to the dissolver so that a maximum amount of scale would be present during the subsequent dissolution of irradiated U metal and during the product extraction and decontamination steps. With the exception of the second run in which about 40% of the Pu was lost in the waste solution of the extraction step, the average waste loss in the other four runs through the extraction and one decontamination cycle was 7.5%. The overall decontamination factors averaged 1700 for the beta activity and 220 for gamma activity. The total Pu losses throughout the extraction step and one decontamination cycle in two additional control runs without scale averaged 2.8%. The average overall decontamination factors in these control runs were 1400 for the beta activity and 240 for gamma activity.(CN-1584). These tests indicate that the presence of scale causes a slight increase in Pu losses but no change in decontamination.

Jacket removal at Hanford will be performed in the same tank that is used for dissolving the U. This metal dissolver is steam-jacketed, has a water-cooling coil inside at the bottom, and has a packed tower on top with a water-cooling coil above it which acts as a reflux condenser. In a tentative jacket-removal procedure given in the Hanford flowsheet dated March 29, 1944 and subject to further investigation, three slug charges (2200 lbs. U each) are loaded into the dissolver and then 20% $HNO_3 + Hg(NO_3)_2$ are added. The temperature is raised to 100°C. by steam and held there about one-half hour until the Al is dissolved. This solution which contains about 2% HNO_3 is jetted to waste disposal. Next any remaining scale is dissolved by adding 10% NaOH and boiling for 3 to 4 hours. About 360 cu. ft. of H_2 are evolved. This solution is jetted to waste disposal. Then a final water wash is added and is also jetted to waste disposal.

Metal Solution

The dissolution of the U in the dissolver is carried out by adding 60% HNO_3, heating to 100-115°C., holding above 105°C. until the specific gravity of the solution reaches 1.75. Then the solution is diluted with water to 40% UNH to prevent freezing. In the dissolution of U considerable gas is evolved. The Hanford flowsheet (March 29, 1944) shows 5800 cu. ft. of NO, 3070 cu. ft. NO_2 and 520 cu. ft. of H_2O per 220 lbs. of active U. In addition, a very small amount of radioactive gases, Xe and I_2, are released. All of these off-gases pass through a packed column and a water-cooled condenser on top of the dissolver and are vented to a main stack, where they are diluted with air to prevent a health hazard to people in the vicinity.

Other solution methods for the U metal have been tried in the laboratory. A higher concentration of HNO_3(69%) causes a faster solution rate but also faster liberation of the off-gases and reaction heat.

Hydrochloric acid will dissolve the U faster than HNO_3 but causes greater corrosion of the equipment. The U is essentially insoluble in H_2SO_4 but the dissolution rate could probably be increased by adding oxidizing agents as H_2O_2, HNO_3 or $K_2Cr_2O_7$. Uranium does not dissolve appreciably in hot 50% NaOH.

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TABLE II

LABORATORY TEST RESULTS ON JACKET REMOVAL

Bond	Chemicals in Order of Addition by Steps	Off Gases by Steps	Uranium Loss	Scale Removal	Total Hours*	Remarks
Al-Si	(1) 10% HNO_3 + Hg**	(1) NO + H_2(?)***	0	Slight	4	Large volume of acid
"	(1) 10% HNO_3 + Hg successive batches, (2) 5% HNO_3 + Hg final	(1) NO + H_2(?)	< 0.5%	100%	20	" " " "
"	(1) 10% HNO_3 + Hg (maintain strength by additions of 60% HNO_3), (2) 5% HNO_3 final	(1) NO + H_2(?)	< 0.5%	100%	20	" " " "
"	(1) 10% HNO_3 + Hg, (2) 10% HNO_3 + Hg + 1N HF			Ppt Film (UF_4?)	3	
"	(1) 10% HNO_3 + Hg, (2) 1N HF			Ppt Film (UF_4?)	9	
"	(1) 10% NaOH	(1) H_2		Slight	3	Largest gas volume
"	(1) 10% HNO_3 + Hg, (2) 10% NaOH, (3) 10% HNO_3 + Hg	(1) NO + H_2(?), (2) H_2	0.3%	100%	8	
"	(1) 10% HNO_3 + Hg, (2) 50% NaOH + 30% H_2O_2	(1) NO + H_2(?), (2a) H_2 (2b) O_2	< 0.1%	Partial	7	
"	(1) 20% HNO_3 + Hg, (2) 10% NaOH	(1) NO + H_2(?), (2) H_2				W flowsheet dated 3/29/44
"	(1) NaOH + $NaNO_3$	(1) NH_3 + H_2	0	Slight	3	Low gas volume
"	(1) NaOH + $NaNO_3$, (2) 10% HNO_3 + Hg	(1) NH_3 + H_2	0.3%	100%	5	" " "
"	(1) 10% HNO_3 + Hg, (2) NaOH + $NaNO_3$, (3) 10% HNO_3 + Hg	(1) NO + H_2(?), (2) NH_3 + H_2	?	100%	8	" " "
"	(1) H_3PO_4(concentrated)·(180-200°C)	(1) H_2	~8%	100%	1	Large gas volume
Zn-Sn	(1) 10% HNO_3 + Hg	(1) NO + H_2(?)			$1\frac{1}{2}$	Forms insoluble metastannic acid
Zn	(1) 10% HNO_3 + Hg	(1) NO + H_2(?)	0.3%	100%	4	
None	(1) 10% HNO_3 + Hg	(1) NO + H_2(?)	0.3%	100%	4	

The above tests were run with boiling solutions, except with HF for which room temp. was used.

* Based on $\frac{1}{4}$" aluminum end caps

** 0.1% $Hg(NO_3)_2$ catalyst

*** H_2 may be evolved if no free HNO_3 present. Reaction might be $2Al + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2$ (Hg catalyst)

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PRECIPITATION PROCESSES

The precipitation processes for the separation of Pu consist of a succession of precipitations in which Pu and fission products are co-precipitated with inactive compounds, such as $BiPO_4$ and LaF_3, which act as "carriers". This technique is employed because the Pu and fission products are not usually present in sufficient concentrations to be precipitated directly. These carriers are selected so that Pu is co-precipitated or "carried" in only one of its oxidation states. The precipitation conditions are regulated so that a minimum quantity of fission products is carried simultaneously with Pu and a substantial fraction is carried when Pu is not co-precipitated. Sometimes "scavengers" and "hold-back" agents are employed to improve decontamination. Scavengers are inactive compounds added during by-product (fission product) precipitation steps that co-precipitate with the carrier to increase the removal of fission products. Hold-back agents are inactive compounds added during the product precipitation steps to decrease the amount of fission products carried with the Pu.

A typical precipitation process consists of extraction, decontamination, concentration and isolation steps. In the extraction step Pu is separated from the U solution. A pre-reduction step is required before the extraction if this precipitation must be made from a reduced solution. The decontamination step consists of a series of precipitations to reduce the gamma activity by a factor of 10^5-10^6. The concentration cycle not only concentrates the Pu solution but also gives an additional decontamination of about 10^2. A total gamma decontamination of at least 10^7 before the isolation step is required. In the isolation step the Pu solution is concentrated further and purified.

The various precipitation processes are discussed below. Complete processes have not been developed for many of the carriers, but they have been included here to provide a complete record of precipitation process development work. Since an endless number of couplings is possible, only the principal ones have been mentioned. The most important process, of course, is the present one for Hanford, and it is described first.

Bismuth Phosphate - Lanthanum Fluoride

The $BiPO_4$ - LaF_3 process is based on the fact that a precipitate of $BiPO_4$ carries Pu in the reduced state and not in the oxidized state. The concentration of H_3PO_4 and the presence or absence of Fe(III) are the principal variables influencing the percent of fission products carried by $BiPO_4$. Since Cb and Zr are complexed by H_3PO_4, high concentrations of this acid are used in product precipitation to minimize the co-precipitation of these elements and low concentrations of this acid are used in by-product precipitation to facilitate their co-precipitation. Lanthanum, the remaining principal fission element to be removed in decontamination, is not complexed by H_3PO_4. The co-precipitation of La with Pu is minimized by the presence of Fe(III) which acts as a hold-back agent. The Fe(III) is present from the reducing agent, Fe(II), added previous to the product precipitations in the decontamination cycle. Only an insignificant amount of Fe is carried over to the by-product precipitation to interfere with the co-precipitation of La there.

The $BiPO_4$ - LaF_3 process is the main line process operated at Clinton and to be operated at Hanford. A flowsheet condensed from the one issued by J. B. Work, March 29, 1944, is attached at the end of this report, Figure 1. The following discussion of the Hanford process is based on this flowsheet.

Status: The status of the Hanford process as of June 1, 1944 may be summarized as follows. This process appears to be operable at Hanford concentrations. Considerable effort is now being expended to improve yields and decontamination. Laboratory work now in progress with scavengers will probably show that a two-cycle decontamination process is feasible and will give the desired gamma factor of 10^5-10^6 before the concentration cycle. The isolation step has been developed but not fully proved.

Pre-reduction: Since the Pu is to be co-precipitated with $BiPO_4$ in the extraction step, it is necessary that it be reduced. The Pu which has been partially oxidized by HNO_3 during the metal dissolving step is reduced with HCOOH at 100-105°C. Allowing the temperature to fall below 100°C. causes an undesirable accumulation of unreacted HCOOH. The HCOOH also neutralizes excess HNO_3 from the dissolving step. In plant operation, a HNO_3 analysis is made to determine the amount of HCOOH to be added; however, a small amount of free HNO_3 (under 0.5%) usually remains. In laboratory tests (CN-1700) with ten times Hanford Pu concentrations, rapid oxidation of Pu(IV) to Pu(VI) occurred at 75°C. in 20% UNH - 0.2 N HNO_3. For this reason it has been suggested that the present HCOOH pre-reduction which requires heating to about 100°C. be discontinued in favor of an alternate reduction process such as $NaNO_2$ which takes place at room temperature.

Alternate methods of pre-reduction have been tried in the laboratory. Replacing HCOOH with 0.01 M uranous ion resulted in high waste losses in extraction. The addition of 0.1 M $NaNO_2$ to the extraction solution completely reduced Pu(VI) to Pu(IV) in 5 minutes at room temperature in further laboratory tests with ten times Hanford concentration of Pu. Hydroxylamine also rapidly reduced Pu(VI) but produced considerable Pu(III) which is not carried as well by $BiPO_4$ as is Pu(IV). Several hours at 75°C. were required for complete reduction of Pu(VI) by HCOOH and $H_2C_2O_4$(Mn catalyst).

Although complete reduction of the Pu is essential for good yields in extraction, it apparently is not always necessary that this be entirely accomplished in the pre-reduction step. Innumerable cases in which the Pu was incompletely reduced by a HCOOH, U(IV), or $NaNO_2$ pre-reduction treatment gave negligible losses in subsequent extractions. This is accounted for by a shift in the Pu(IV)/Pu(III) potential on addition of H_3PO_4 or H_2SO_4 (after pre-reduction and prior to extraction) and the presence of residual reducing matter. Thus if all the Pu(VI) is not reduced by HCOOH, the remainder may still be reduced during the $BiPO_4$ precipitation and digestion and the extraction yield may be high.

Extraction: The purpose of the extraction step is to separate the Pu from U and as much fission activity as possible. A gamma decontamination factor of about 12 is obtained. In this step the solution is first diluted to 20% UNH concentration and then made 1 M in H_2SO_4. The latter prevents U from precipitating with the $BiPO_4$ by forming a complex uranium sulfate that cannot be converted to the insoluble phosphate. The solution is heated to 75°C. and a direct strike made by adding first $BiONO_3$ (2.6 g. Bi^{+3}/l.) and then H_3PO_4 to a concentration of 0.75 M. This forms a $BiPO_4$ precipitate which carries the Pu. After digesting for 2 hours at 75 C., the solution is cooled to 35°C. and centrifuged. The cake is washed three times with H_2O and the washings together with filtrate containing U and fission activity are jetted to waste disposal. The plutonium-containing cake is dissolved by adding 48% HNO_3.

One critical point in this extraction step is the degree and type of agitation. Laboratory tests have shown that the loss of Pu in the waste solutions decreases with increased power input, but a sound basis for comparing laboratory and plant results has not been established. In the Clinton plant, power inputs of 1.1 HP per 1000 gallons slurry gave waste losses of about 1%.

In laboratory tests (CN-1429) the temperature of strike and digestion during extraction had little effect on yield between 55 and 90°C., but below 55°C. the waste losses increased appreciably. With 1-hr. digestion times the Pu waste losses were 5.0, 5.0, 5.3 and 12.1% at 90, 75, 55 and 35°C. respectively. With a 2-hr. digestion time the Pu waste losses were 4.5, 3.8 and 9.1% at 75, 55 and 35°C. respectively.

The amount of Bi and Pu adhering to the walls of the stainless steel laboratory extraction precipitator was found to be decreased with decreased strike and digestion temperatures. The percentages of total Pu adhering were 27.5, 25.3 and 17.3% at 90, 75 and 55°C. respectively. The percentages of total Bi adhering were 28.6 , 19.4 and 18.0% at the same respective temperatures. Since these percentages of Pu and Bi are roughly equivalent, this indicates that the $BiPO_4$ precipitate carrying Pu is retained on the walls of the precipitator rather than Pu being absorbed on the walls. Anodizing the surface of the stainless steel beaker used for precipitations reduced the hold-up of Bi and Pu from 15-30% to 5-15%. The presence of Fe from corrosion in amounts over 0.02 N decreases the carrying power of $BiPO_4$ in the presence of U.

Concentration variables in the extraction step were also studied in the laboratory. Nitric acid concentration up to 5% had little effect on Pu waste losses with the usual 2-hr. digestion time. With a 1-hr. digestion time, the waste losses increased slightly with increased HNO_3 concentration. The amount of Pu in the wastes with 1-hr. digestion times was 5.1, 7.4, 6.8 and 7.1% at HNO_3 concentrations of 1.5, 2.5, 3.0 and 5.0% respectively. Concentrations of UNH below 20% result in only a minor decrease in waste loss. Concentrations above 25% result in larger waste losses. With a 1-hr. digestion time the percentage of Pu in the waste was 4.2, 5.0, 7.1, 16.0 at UNH concentrations of 10, 20, 25 and 30% respectively. The waste losses decreased with increasing amounts of Bi through the range of 1.25-3.0 g. Bi^{+3}/l. With Bi concentrations of 1.25, 2.0, 2.5, and 3.0 g. Bi^{+3}/l. the Pu losses in the wastes were 14.6, 6.0, 3.4 and 1.9% for 1-hr. digestion times and 9.8, 4.1, 2.8 and 1.4% for 2-hr. digestion times.

Other concentration variables investigated in the laboratory were those for H_3PO_4 and H_2SO_4. The Pu waste losses observed when using H_3PO_4 concentrations of 0.4, 0.6, 0.8, 1.0 and 1.2 M were 5.1, 4.6, 5.0, 4.4 and 3.7%

with 1-hr. digestion and 3.9, 5.2, 4.6, 3.8 and 2.5% with 2-hr. digestion respectively. The Pu waste losses decreased as the rate of addition of H_3PO_4 was decreased, keeping the total strike and digestion time constant at three hours. In these tests with strike times of 15, 30, 60 and 120 min. the amount of Pu remaining in solution was 3.0, 2.7, 1.8 and 1.2%. Concentrations of H_2SO_4 between 0.6 N and 1.5 N had no appreciable effect on the Pu waste losses.

Decontamination: The object of the decontamination cycles is to reduce the fission activity until an overall gamma decontamination factor of 10^5-10^6 is obtained. Until this gamma decontamination is reached at Hanford it will be necessary to process the Pu solutions by remote control. After that less shielding will be required on the equipment and there will be greater latitude for operation and maintenance.

One decontamination cycle in the Hanford process consists of a by-product precipitation with Pu in the oxidized state followed by a product precipitation with Pu in the reduced state. The Pu solution from the extraction step is diluted with H_2O to 27% HNO_3, and oxidation is accomplished by adding $NaBiO_3$ and agitating for 1 hour at 50°C. A small amount of $Na_2Cr_2O_7$ is next added as a holding oxidant. The first by-product precipitation is carried out by diluting to 6.1% HNO_3, heating to 75°C., adding H_3PO_4 and digesting for one hour at 75°C. The precipitate is washed twice with H_2O and dissolved with 43% HNO_3 for waste disposal. The filtrate is reduced with $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6 H_2O$, heated to 75°C., and digested for 1 hour. Then the product precipitate is formed by adding $BiONO_3$ solution, digesting 30 minutes at 75°C., then adding H_3PO_4, and digesting 2 hrs. at 75°C. The precipitate is washed three times with H_2O and then dissolved in 48% HNO_3. The filtrate is sent to waste disposal. Because UNH is not present in the decontamination cycles, the agitation and other conditions for the precipitation of $BiPO_4$ are not as critical as in the extraction step. This decontamination cycle is then repeated. A minimum gamma decontamination factor of 10^5 should be reached before the concentration step.

Recent tests indicate that the use of scavengers in the by-product precipitations is necessary in order to obtain sufficient gamma decontamination. In the presence of Hanford concentrations of inactive fission elements the Hanford process without scavengers will not give the required gamma decontamination of 10^5 through extraction and two decontamination cycles. Values of 10^4 were obtained in the laboratory and 10^3 in the semi-works. The presence of Hanford concentrations of Pu did not result in higher gamma decontamination values.

Cerium (IV) and Zr(IV) in combination are very effective as scavengers. Zirconium phosphate alone is difficult to centrifuge, whereas $Ce_3(PO_4)_3$ is not only easily centrifuged but also aids the separation of Zr. The combined precipitate of $BiPO_4$, $Zr_3(PO_4)_4$ and $Ce_3(PO_4)_4$ is not readily dissolved by HNO_3 alone, but the addition of 2-4% H_2O_2 eliminates this difficulty. The H_2O_2 reduces Ce(IV) to Ce(III) forming $CePO_4^{2}$ which is soluble. Zirconium phosphate is not solubilized and remains as a finely divided suspension. These scavengers are most advantageously introduced to the diluted oxidized solution from which all but traces of H_3PO_4 have been removed by excess Bi. Alternate scavengers for the second decontamination cycle that appear promising are TiO_2, $Ce_3(PO_4)_4$-Cb_2O_5, $BaSO_4$-LaF_3. As yet no suitable substitute for LaF_3 has been developed as an alternate rare earth by-product precipitation method.

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The use of scavengers in both decontamination cycles is ideal, providing Pu losses are not excessive. First cycle factors of 10^3 or better have been secured with Ce(IV) and Zr(IV) scavengers in the laboratory (200 mg./. of each), and an overall value of 10^6 results from the use of this combination in two successive cycles. In some tests, however, the use of scavengers has resulted in 1-3% less yield per by-product precipitation as compared to that obtained in an unmodified by-product precipitation. Semi-works tests indicate that these scavengers are operable chemically, but that the same large advantages achieved in the laboratory cannot be secured without elimination of the small percentage of "fines". Higher centrifugation speeds, recentrifugation, or the use of flocculating agents may offer some improvement.

Improved decontamination also appears to be possible through the use of hold-back agents. Of several elements tested as hold-back agents in the extraction step, $Al(NO_3)_3$ was the most effective. This indicates that hold-back agents do not need to be inactive compounds of active fission elements as previously believed.

Concentration: The purpose of the concentration cycle is to reduce the volume of Pu solution to about 8 gallons and secure an additional gamma decontamination factor of about 10^2. The concentration cycle consists of two by-product precipitations, one product precipitation, and finally a metathesis.

Bismuth phosphate is used for the first by-product precipitation. The Pu solution from the decontamination cycles is diluted with water and then oxidized by adding $NaBiO_3$ and agitating one hour at 50°C. A small amount of $Na_2Cr_2O_7$ is then added as a holding oxidant. The oxidized solution is diluted with H_2O to 6.1% HNO_3, heated to 75°C., and a $BiPO_4$ by-product precipitate formed by adding H_3PO_4 and digesting 1 hour at 75°C. The precipitate is washed twice with H_2O, dissolved in 48% HNO_3, and jetted to waste disposal.

The next by-product precipitation is made with LaF_3. In the latest tentative procedure a La solution recycled from a subsequent isolation step is added to the oxidized filtrate. This mixture is oxidized further by adding $NaBiO_3$, and agitated 1 hour at 50°C. After adding a small amount of $Na_2Cr_2O_7$, the solution is cooled to 25°C. and a LaF_3 precipitate formed by adding anhydrous HF and digesting 1 hour at 25°C. The precipitate is centrifuged and washed twice with $HF-HNO_3$ solution. The cake is slurried with H_2O to waste.

Lanthanum fluoride is used for the product precipitation, which is performed in two steps. The oxidized filtrate is adjusted to 35°C., reduced by adding $H_2C_2O_4$ with $Mn(NO_3)_2$ as a catalyst. After digesting 1 hour at 35°C. the first LaF_3-product precipitate is formed by adding $La(NO_3)_3 \cdot 2\ NH_4NO_3 \cdot 4\ H_2O$ and digesting 1-1/2 hours at 35°C. The precipitate is centrifuged and a second precipitate made by adding the La salt again and digesting 1-1/2 hours at 35°C. After centrifuging again the cake is washed twice with $HF-HNO_3$. The filtrate is sent to waste disposal and the cake slurried with H_2O to the next cell for metathesis.

LaF_3 precipitates are finely divided and difficult to separate in the plant centrifuge. For satisfactory Pu recovery, it is necessary to centrifuge at high speed, precipitating the LaF_3 in two portions and centrifuging

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twice. Laboratory tests have shown that the centrifuging characteristics of LaF_3 may be significantly improved by the addition of flocculating agents and this observation has been confirmed by high spot tests in the Clinton semi-works and plant.

The purpose of the metathesis step which is performed next in the concentration cycle is to convert the difficultly soluble fluorides to hydroxides which can be readily dissolved in HNO_3. For metathesis, KOH is added to the LaF_3 slurry and then this slurry (15% KOH) is held at 75°C. for 1 hour. After cooling to 35°C. the slurry containing $La(OH)_3$ and $Pu(OH)_4$ is centrifuged and the filtrate sent to waste. The cake is slurried from the centrifuge to the tank and KOH is added again to insure complete metathesis. After agitating 1 hour at 35°C. the solution is centrifuged again and the filtrate sent to waste. The cake containing Pu is dissolved in 25% HNO_3 and then divided into 3 portions for isolation. Tank metathesis with 15% KOH concentration has given good results in the Clinton plant and is now standard practice. Formerly, metathesis was performed in a centrifuge. Advantages of the tank procedure are: less exposure of the operator to radiation, less wear and tear on the centrifuge, and simplified operation.

Various metathesis procedures have been tested in the laboratory. A reaction time of one hour at 75°C. is usually adequate with 15% KOH, but at lower KOH concentrations the time must be correspondingly increased. It has been shown that KOH is superior to NaOH for metathesis. Recent laboratory tests have indicated that improvement in metathesis can be secured by including 10% K_2CO_3 in the 15% KOH solution. Also, the dissolution of the fluoride precipitate in 45% K_2CO_3 alone and subsequent precipitation of hydroxides by KOH gave good results. This last method provided better Fe removal and subsequent lower peroxide solubility in the isolation step, but it is a more complicated procedure.

An alternate method of concentration under investigation in the laboratory consists of dissolving the final product precipitate of the decontamination cycle in HCl, and making a $U(C_2O_4)_2$ precipitation. The $U(C_2O_4)_2$ product precipitate is formed by adding 1 mg./ml. of U(IV) to the HCl (5 $\underline{N}$) solution containing 50 mg./ml. Bi(III) as $BiPO_4$, 0.4 $\underline{M}$ $H_2C_2O_4$, 0.1 $\underline{M}$ KCl and 0.04 mg./l. Pu. Laboratory yields of 94% and 87% were obtained with Fe(III) present at 0.05 $\underline{M}$ and 0.10 $\underline{M}$ respectively. The deleterious effect of Fe was more marked at higher Bi(III) concentrations. When potassium was absent, the carrying of tracer Pu by $U(C_2O_4)_2$ was less than 40%, and thus traces of potassium are apparently necessary for good yields. In a subsequent test a 95% yield was obtained with a sample from a semi-works solution containing 120 mg./ml. Bi(III) as $BiPO_4$, 5 $\underline{N}$ HCl, 0.05 $\underline{M}$ Fe(III), 0.4 $\underline{M}$ $H_2C_2O_4$, 0.1 $\underline{M}$ KCl, 0.007 mg./l. Pu. The U(IV) was added in two shots of 0.5 mg./ml. each, and it was not necessary to remove the first precipitate before bringing down the second.

The $U(C_2O_4)_2$ product precipitate in this alternate concentration method can be dissolved in HNO_3-$K_2Cr_2O_7$ or K_2CO_3-H_2O_2 solutions. The U(IV) is oxidized to U(VI) as UO_2(II) by adding the oxidizing agents, whose excess must be destroyed to prevent subsequent oxidation of the U(IV) added for the second $U(C_2O_4)_2$ precipitation. Any Pu which has been oxidized in these steps must be reduced. After dissolving the first $U(C_2O_4)_2$ precipitate and diluting to about 10% UNH, there is a strong tendency for $UO_2C_2O_4$ to precipitate, even in the presence of 4 N HNO_3. The addition of 3 N HCl prevented this $UO_2C_2O_4$ precipitation. The solution for the second precipitation can contain about 10% UNH and 6 N HNO_3. The yields in this second $U(C_2O_4)_2$ precipitation have been low, usually 80% or less. $U(C_2O_4)_2$ is generally unfilterable and does not settle rapidly. A centrifuge, resistant to HCl, would be required. The principal disadvantages of the $U(C_2O_4)_2$ concentration method are (1) the use of HCl, which is very corrosive, and (2) poor yields in the second precipitation. These disadvantages seem to outweigh the advantage of large volume reductions (80-12,000).

Another concentration scheme involves precipitating LaF_3 from the $BiPO_4$-HCl solution after the decontamination cycle. With this method a 96% yield has been obtained.

Preliminary laboratory studies have been made on a Cb_2O_5-LaF_3 concentration method. Two LaF_3 precipitations and one intervening Cb_2O_5 precipitation gave an overall yield of 81% for tracer amounts of Pu. About one-half of the loss occurred in washing the Cb_2O_5 precipitate and most of this might be eliminated by suitable modifications of technique.

In an alternate $Bi(OH)_3$ concentration method, the $BiPO_4$-HNO_3 solution from the decontamination cycle is diluted from 10 N to 3.4 N HNO_3 and rendered alkaline by the addition of solid KOH. This bulky white precipitate was digested for 1 hour at room temperature and washed twice with 0.01 N KOH. The precipitate was dissolved in 16 N HNO_3, and the solution diluted, heated to 55°C. and treated with 10% excess H_2O_2, and the resulting PuO_4 digested for 3 hours at 55°C. This last step is really a part of the isolation procedure. Although this is a promising method, laboratory results so far have given low yields.

Numerous other concentration methods have been considered, but the work on them has been largely of an exploratory nature. Some of these methods are described later in this report under their respective carriers.

Isolation: The purpose of the isolation step is to produce a Pu compound with satisfactory purity and in a concentrated solution. This step consists of two PuO_4 precipitations. This isolation method should be considered tantative only and has not been proved. Both Fe and Zr are known to interfere. If the peroxide cannot be formed so as to be consistently filtered or settled it will be necessary either to provide centrifuges or develop another isolation compound that can be filtered or settled. Work is in progress to improve the filtration properties of peroxide and also to study other compounds.

In the isolation step 30% H_2O_2 is added to the 2-2/3 gallons of solution from the concentration step in four equal portions at 15 min. intervals with vigorous agitation. After additional agitating for one hour, the slurry is filtered on sintered glass, and the PuO_4 is washed twice with a HNO_3-H_2O_2 solution. The filtrate plus washings are returned to the concentration cycle. The PuO_4 is dissolved in 70% HNO_3 at 75°C. and after 1/2 hour washed through the filter with cold water. A second PuO_4 precipitation is then made in the same manner. This precipitate is dissolved in HNO_3 as before, and the final solution is put into a container for shipment to the purification laboratory. This final solution (2.8 liters) contains about 80 grams of Pu as $Pu(NO_3)_4$.

Iron and Zr are the principal interferent impurities in the direct peroxide precipitation of Pu from LaF_3 metathesized solutions in the isolation step. PuO_4 is decomposed by $Fe(NO_3)_3$ solution, but its interference with precipitated peroxide is not serious if the concentration of Fe(III) is less than 0.05 M and the time of contact does not exceed 3 hours. However, Zr is a serious problem, particularly if present in combination with Fe. Precipitation of the peroxide is inhibited completely by the presence of 10 mg./ml. of Zr(IV), and satisfactory product yields were not obtained when the Zr(IV) concentration exceeded 0.1 mg./ml. Zirconyl nitrate has been used at Clinton to complex any unmetathesized LaF_3 that is present. It may be necessary to use this at Hanford. In such a case the concentration of Zr(IV) should not exceed 0.1 mg./ml. of product solution sent to the isolation cycle.

In recent laboratory tests on the isolation step the presence of 0.2 N H_2SO_4 has been shown to aid in precipitation. The conditions of precipitation which appear to result in readily filterable PuO_4 are 0.2 N H_2SO_4, 60°C., 10% excess H_2O_2 added over a period of 1 hour, 2 hours digestion at 60°C. In this case the upper tolerable limit of Fe(III) concentration is 0.002 M. Both the first and second PuO_4 precipitates have been filtered satisfactorily. Some difficulty has been encountered in dissolving the precipitates and further work on this is in progress. The presence of Mn(II) impurity in concentrations up to 70 mg./ml. seems to have no effect on Pu yield. The presence of Cr(III) impurity in concentrations of 40 mg./ml. and higher decreases the yield.

Reducing Agents: A number of reducing agents have been used for the various reduction steps in the Hanford process. The use of Fe(II), U(IV), and $H_2C_2O_4$ as reducing agents in the decontamination cycle resulted in decontamination factors in the ratio 20:9:1. The favorable effect of Fe may be due to its ability to inhibit fission product carrying by the product precipitate. Poor decontamination with $H_2C_2O_4$ may be due to precipitation of some $Bi_2(C_2O_4)_3$ along with the $BiPO_4$. Oxalic acid with Mn(II) as a catalyst provides complete reduction in 1 hour at 35°C. in the concentration cycle. This low temperature is desirable to minimize corrosion by HF. Formerly the reduction at this point was made with H_2O_2. Reducing agents for the metal solution are described under a previous section, "Pre-reduction".

Oxidizing Agents: Of the various oxidizing agents tried for the Hanford process $NaBiO_3$ has been chosen as the standard oxidant. Oxidation is secured in 1 hour at 50°C. Other oxidants, however, are being investigated in the laboratory so that an alternate will be available if necessary. Satisfactory conditions for oxidation with Pb_3O_4 are 1 hour at 50°C. with 0.02 M Pb_3O_4 and 5 N HNO_3 concentrations. The completeness of oxidation is relatively insensitive to changes in any single variable. The cost of Pb_3O_4 is about 1/10 that of $NaBiO_3$. It appears that PbO_2 might be a satisfactory oxidizing agent at high temperatures (75°C.) and in the presence of MnO_4^- catalyst (10^{-4} M).

Bismuth tetra-oxide appears to oxidize Pu quantitatively at room temperature and without a catalyst. About 95% oxidation was obtained with $Pb(C_2H_3O_2)_2$ at both 50°C. and room temperature. With additional investigation, conditions for complete oxidation probably could be found. Cerium (IV) oxidized Pu(IV) to Pu(VI) within 15 minutes at room temperature. Potassium dichromate at room temperature is a poor oxidizing agent for producing Pu(VI), but it appears to be good as a holding oxidant and is used in this way in this process.

Yields: The yield results obtained from both laboratory and plant scales of operation at Clinton have shown that the extraction step is capable of producing about a 98-99% yield. The average Pu loss in U waste for 102 Clinton plant runs is 1.6%. Occasionally unpredictable high losses (4-6%) have occurred which could not be correlated with residual HNO_3 concentration or aging time of the UNH. A study of $BiPO_4$ precipitation variables indicated that yields decrease with

(1) decreased agitation
(2) decreased temperature (below 55°C.)
(3) decreased Bi concentration (below 2.5 gm./l. Bi)
(4) increased UNH concentration (above 25%)
(5) increased rate of striking

Variations in UNH solutions, however, have caused greater differences in yields than changes in some of the above variables. It may be that these variations are dependent upon the effectiveness of the preliminary HCOOH treatment.

High yields have been obtained for the decontamination and concentration steps also. The average yieldsin the first $BiPO_4$ by-product precipitation based on 73 Clinton plant runs is 98.9%. In the last 35 of these runs (#84-118), an average yield was 99.4%. The average yield in the last 35 Clinton plant runs (#84-118) in the second $BiPO_4$ by-product precipitation was 99.6%. Laboratory tests (CN-1643) at Hanford concentrations of product and inactive fission products gave average $BiPO_4$ by-product precipitation yields of about 99.6% and $BiPO_4$ product precipitation yields of about 99.4%. The average laboratory yields in the LaF_3 by-product and product precipitations in the concentration cycle were 99.5% and 98.9% respectively.

Isolation experiments in the laboratory indicate that an overall yield for this step of 96% is possible and may reach 98-99% (CN-1700). When the peroxide supernatants are recycled, however, there is no Pu loss in the isolation step.

The following table on yields is based on the above data and indicates a possible overall yield for Hanford of about 93% when no scavengers are used.

Table III

Estimated Hanford Yields
No Scavengers Used

Step	% Yield
Extraction	98.4
Decontamination	
$BiPO_4$ By-product	99.4
$BiPO_4$ Product	99.4
$BiPO_4$ By-product	99.6
$BiPO_4$ Product	99.4
Concentration	
$BiPO_4$ By-product	99.6
LaF_3 By-product	99.5
LaF_3 Product	98.9
Metathesis	98.5
Isolation (Peroxide supernatants recycled)	100
Overall Yield	93

Waste Disposal: The U waste solution from the extraction step contains nearly 90% of the fission activity. It is not planned to decontaminate this solution, but equipment has been installed so that this can be done to some degree if it is later found necessary. The solution is neutralized by adding 30% Na_2CO_3 slowly enough to prevent pressure buildup in the precipitator. Since the 30% Na_2CO_3 freezes at 30°C., blasts of steam are sent through the pipes before and after its transfer. Lower concentrations of 20% and 25% Na_2CO_3 offer no advantage because they freeze respectively at 21°C. and 26°C. and would increase the waste volumes. The Na_2CO_3 forms a soluble complex U salt. Neutralization with NaOH would form a heavy yellow precipitate which might be difficult to remove. Neutralization minimizes corrosion in the transfer lines and storage tanks. The solution is stored in buried concrete tanks. Since the high activity will cause the solution to boil, the tanks are fitted with large air-cooled reflux condensers.

The Al jacket solution and decontamination wastes contain about 10% of the original fission activity. These are neutralized with NaOH and sent to buried concrete storage tanks fitted with small air-cooled condensers.

The wastes from the concentration cycle are also neutralized with NaOH and then sent through settling tanks to remove any solids. From there they enter large retention basins where they are diluted with process H_2O. The liquid overflowing from these basins has essentially no activity.

Bismuth Phosphate

The $BiPO_4$ process is the same as the Hanford process just described except that $BiPO_4$ is used instead of LaF_3 in the concentration cycle. The Hanford process, however, is superior in that it provides greater concentration because a smaller amount of LaF_3 precipitate is required to carry Pu. It has been stated that LaF_3 also provides increased decontamination by removing La and the other rare earths more effectively than $BiPO_4$.

Lanthanum Fluoride

The LaF_3 process is analogous to the $BiPO_4$ process. After prereduction with either HCOOH or U(IV), La (0.25 gm./l) is added to the 20% UNH solution and a LaF_3 product precipitate is formed by making the solution about 1.5 N in HF, maintaining the HNO_3 concentration at 1 N. This precipitate carries Pu and about 50% of the fission products. The precipitate is centrifuged and is normally dissolved by treatment with $ZrO(NO_3)_2$ solution. As an alternate the LaF_3 can be converted to $La(OH)_3$ by metathesis with concentrated KOH, and then the $La(OH)_3$ containing Pu can be dissolved in HNO_3. The resulting solution after the dissolving procedure is oxidized by $Na_2Cr_2O_7$ or $NaBiO_3$. After oxidation, a by-product precipitate is made by adding HF. This precipitate removes most of the fission product activity which was carried in the extraction step. The solution is then reduced with Fe(II), H_2O_2 or $H_2C_2O_4$. Lanthanum nitrate is added slowly to the reduced solution in several portions to give a preformed precipitate of LaF_3 which carries Pu. Further decontamination is secured by successive oxidation-reduction cycles as outlined above. The concentration cycle for this LaF_3 process is similar to that described for the Hanford process. The LaF_3 product precipitate is centrifuged, metathesized and dissolved in HNO_3. The Hanford isolation step as previously described then follows.

This process has also been tested using an extraction step in which a LaF_3 by-product precipitate is removed in the presence of U and the solution reduced with arsenite before separating Pu from U. This method is not so desirable as the one described above, because the reduction step must be made in the presence of U which makes the choice of reducing agents rather critical in that many which are satisfactory for Pu reduction also reduce U(VI) to U(IV) ion. The U(IV) so formed also precipitates with HF.

Another variation in this process involves the use of Ce as a complexing agent for the LaF_3. The initial product precipitate of LaF_3 from the 20% UNH solution can be complexed with Ce(IV). The Ce(IV) like Zr(IV) will complex LaF_3 so it can be dissolved at room temperature. Simultaneously, the Ce(IV) oxidizes Pu. Next KNO_3 and HF are added to make by-product precipitates of CeF_3 and CeF_4. The oxidized solution can then be reduced with Fe(II). The above system, however, has been unsuccessful in that erratic results in oxidation with Ce(IV) have been obtained in the presence of stainless steel. The addition of a strong oxidizing agent as $NaBiO_3$, however, might eliminate this difficulty.

Some of the advantages of the LaF_3 process as an alternate for the Hanford process are:

1. It has been highly developed in the laboratory and semi-works.
2. Lanthanum fluoride carries Pu at all concentrations from many solutions.
3. It has been used successfully in the concentration step at the Clinton plant.
4. It can be used in the present Hanford equipment.
5. Precipitation of LaF_3 from solutions of $BiPO_4$ and precipitations of $BiPO_4$ from solutions of LaF_3 has been worked out so that LaF_3 could be introduced into start, middle or end of $BiPO_4$ process.

A possible limitation on this process is that the use of HF requires operation below 45°C. in order to minimize corrosion and obtain satisfactory equipment life.

Sodium Uranyl Acetate

The $NaUO_2Ac_3$ process differs from the $BiPO_4$ and LaF_3 processes in that Pu is carried in the oxidized rather than reduced state. The Pu oxidized in the dissolving step is first reduced with NH_2OH. The NaAc is added to precipitate the bulk of the U present, which is centrifuged or filtered and discarded. The solution is acidified with HNO_3 and oxidized with $Na_2Cr_2O_7$ by heating one hour at 75°C. Next NaAc and $NaNO_3$ are added to give a 5 N $NaNO_3$ concentration and a ratio of about 1:1 of HAc to NaAc (about 0.2 to 0.5 N Ac concentration). The U remaining in solution from the first step precipitates as $NaUO_2Ac_3$ carrying the Pu and leaving most of the fission products in solution. Further decontamination may be obtained, without oxidation-reduction cycles, by merely dissolving the product precipitate in 0.5 N HNO_3 and re-precipitating with $NaUO_2Ac_3$. Successive oxidation-reduction cycles can then be carried out for additional decontamination and also concentration.

This process has not been tested in semi-works and has the disadvantage of requiring extremely large amounts of process chemicals. Also, the very large extraction precipitate in the first step is a handicap. Several possible improvements in this process are being investigated. Couplings to other carriers and also an adsorption process are described later.

Bismuth Arsenate

Bismuth arsenate carries Pu to about the same extent as $BiPO_4$ at Hanford concentrations and is probably more filterable. It is slightly more insoluble and requires more HNO_3 for dissolving it; consequently, less Bi is used in precipitation. It is probable that an overall process for separating Pu by $BiAsO_4$ can be developed, but only the extraction step has been studied.

Bismuth Arsenate - Bismuth Phosphate

The $BiAsO_4$ - $BiPO_4$ process differs from the $BiPO_4$ process in that $BiAsO_4$ is used for extraction rather than $BiPO_4$. The reduced 20% UNH solution is made 1 N in HNO_3 and about 0.1 M in H_3AsO_4. The product precipitate is then formed by adding Bi(III) (1.5 mg./ml.) to the hot (75°C.) solution and digesting 1-2 hours. The $BiAsO_4$ is centrifuged or filtered. In contrast to the $BiPO_4$ process, no H_2SO_4 is needed to complex the UO_2 ion in the extraction solution because $(UO_2)_3(AsO_4)_2$ is more soluble than $(UO_2)_3(PO_4)_2$ and does not precipitate under the above conditions. The presence of Fe(III) in concentrations of 0.01 M has no effect on the carrying of Pu, but 0.02 M Fe(III) reduces carrying of Pu to 70%, and 0.03 M Fe(III) prevents $BiAsO_4$ precipitation altogether. The $BiAsO_4$ is dissolved in 10 N HNO_3 and oxidation with $NaBiO_3$ is carried out in 5 N HNO_3. The process then becomes identical with the $BiPO_4$ process.

The use of $BiAsO_4$ may prove to have several advantages over $BiPO_4$ for extraction. With the $BiPO_4$ method the HNO_3 concentration of UNH solutions must be maintained at such a low value that the rate of solution of the U metal is very low. With $BiAsO_4$ the HNO_3 concentration of 20% UNH solution may be as high as 1 N Extraction steps by this method followed by $BiPO_4$ decontamination cycles gave higher yields than the regular $BiPO_4$ process, apparently because Zr and Cb originally present at W concentrations did not precipitate as arsenates and remain insoluble in the 5 N HNO_3 used in the oxidation step. The solubilities of $Zr_3(AsO_4)_4$ and $Cb_3(AsO_4)_5$ are believed to be higher than those of corresponding phosphates. The presence of such insoluble precipitates is believed to lead to Pu loss in the first by-product precipitation.

Bismuth Phosphate - Sodium Uranyl Acetate

The $BiPO_4$ - $NaUO_2Ac_3$ process consists of a $BiPO_4$ extraction and one $BiPO_4$ by-product precipitation, followed by $NaUO_2Ac_3$ precipitations for subsequent decontamination and concentration cycles. The use of $BiPO_4$ for extraction avoids the very bulky precipitate involved in the first step of the regular $NaUO_2Ac_3$ process. The oxidized solution from the by-product precipitate is freed of phosphate by adding an aquivalent amount of Zr ion. The $NaUO_2Ac_3$ is precipitated to carry oxidized Pu by adding $UO_2(NO_3)_2$, NaAc, and $NaNO_3$. Further decontamination is accomplished according to the regular $NaUO_2Ac_3$ process. This combination process has had only preliminary laboratory study and the coupling may be critical.

Uranous Oxalate

Uranous oxalate carries Pu in the reduced state. Apparently no overall separation process for this carrier has been developed. The $U(C_2O_4)_2$ alternate concentration method for the Hanford process has been previously described. Couplings to adsorption systems will be mentioned later. Further use of $U(C_2O_4)_2$ is described in the next two processes.

Uranous Oxalate - Sodium Uranyl Acetate

The $U(C_2O_4)_2$ - $NaUO_2Ac_3$ process consists of an extraction step with $U(C_2O_4)_2$ followed by $NaUO_2Ac_3$ precipitations for decontamination and concentration. In the extraction step $K_2C_2O_4$ is added to a 10% UNH solution after the metal dissolving step, giving a $K_2C_2O_4$ concentration of about 7 mg./ml. Uranous sulfate is then either added slowly or in two equal portions without separating the precipitate between each addition. Uranous oxalate separates at room temperature carrying Pu and probably a high proportion of rare earth fission products. Yields of 98% at W concentration have been obtained in the laboratory. The $U(C_2O_4)_2$ product precipitate is crystalline and is separated by filtration or centrifugation and dissolved in 2 N HNO_3-0.2 M $Na_2Cr_2O_7$ solution, which destroys the oxalate ion and converts U(IV) to U(VI). Further treatment with $Na_2Cr_2O_7$ for 2 hours at 75°C. oxidizes the Pu, which is then precipitated with $NaUO_2Ac_3$ as carrier in subsequent decontamination cycles.

It is likely that $U(C_2O_4)_2$ could also be used to carry Pu from solutions of $NaUO_2Ac_3$ in HNO_3 after a reduction of Pu is made. The $U(C_2O_4)_2$ carries the rare earth fission products fairly completely, but probably does not carry appreciable amounts of Zr and Cb, which have been found to interfere with decontamination by the $NaUO_2Ac_3$ process. Since $NaUO_2Ac_3$ does not carry any of the fission products to an appreciable extent except where concentrations of Zr and Cb are high, or in certain cases where the concentrations of impurities are large, very good decontamination and, incidentally, high concentrations should be obtained by a procedure where alternate precipitations of Pu are made with $U(C_2O_4)_2$ and $NaUO_2Ac_3$.

Bismuth Phosphate - Uranous Oxalate - Sodium Uranyl Acetate

The $BiPO_4$ - $U(C_2O_4)_2$ - $NaUO_2Ac_3$ process consists of a $BiPO_4$ extraction and a $BiPO_4$ by-product precipitation, a $U(C_2O_4)_2$ product precipitation, and then as many $NaUO_2Ac_3$ precipitations as are necessary for subsequent decontamination and concentration. The solution containing Pu from the $BiPO_4$ by-product precipitation is reduced with 0.4 $\underline{M}$ $H_2C_2O_4$ in the presence of 0.1 $\underline{M}$ H_3PO_4 and 1.0 $\underline{N}$ HNO_3 by heating 1 hours at 75°C. Then a product precipitate of $U(C_2O_4)_2$ is made by adding a solution of U(IV) in two shots at 1/2-hr. intervals with 1-hr. digestion at room temperature. The presence of 0.03 $\underline{M}$ Fe(III), however, would cause failure of this method, because the precipitate would redissolve after digestion. The $U(C_2O_4)_2$ product precipitate is both dissolved and completely oxidized with 2 $\underline{N}$ HNO_3 - 0.2 $\underline{M}$ $Na_2Cr_2O_7$ by heating 1 hour at 75°C. Subsequent dilution and addition of NaAc to give a solution 0.1 $\underline{M}$ in $Cr_2O_7^{--}$, 0.4 $\underline{N}$ in HNO_3, and 0.6 $\underline{N}$ in HAc, followed by an additional 2 hours at 75°C. results in complete oxidation of Pu. Then a $NaUO_2Ac_3$ product precipitate is made by adding $NaNO_3$ and NaAc.

Columbic Oxide

Columbic oxide carries Pu in the reduced state. The carrying of Pu by Cb_2O_5 has been tested at Hanford concentrations and appears to be satisfactory. Aluminum ion concentration as high as 0.012 $\underline{M}$ has no effect on the carrying, but Fe(III) concentration as low as 0.00005 $\underline{M}$ interferes. Thus the use of Cb_2O_5 as a carrier appears to be very limited, unless other than steel equipment is employed. However, Cb_2O_5 seems to be a good scavenging agent for both active Zr and Cb. A Cb_2O_5 - LaF_3 concentration scheme has been mentioned under the Hanford process. A coupling to $La_2(C_2O_4)_3$ will be described under that carrier. Columbic oxide is also used in the process described next.

Columbic Oxide - Sodium Uranyl Acetate

The Cb_2O_5 - $NaUO_2Ac_3$ process consists of a Cb_2O_5 extraction and by-product precipitation followed by $NaUO_2Ac_3$ precipitations for subsequent decontamination and concentration. Columbic oxide is used to carry Pu from UNH solutions after the metal dissolving step and reduction, providing Fe does not interfere as stated above. The precipitate is dissolved in $H_2C_2O_4$ and an oxidizing agent such as $K_2Cr_2O_7$ or $NaBiO_3$ is added to destroy the oxalate ion and oxidize the Pu. Destruction of the oxalate ion causes precipitation of the Cb_2O_5 which can be removed as a by-product precipitate carrying Cb and Zr fission products. This precipitate is difficult to separate by filtration or centrifugation. After separation of the Cb_2O_5, further decontamination can be secured by $NaUO_2Ac_3$ cycles. This process has not been studied on a semi-works scale.

Thorium Oxalate

Thorium oxalate as a carrier could be readily used in equipment at X and W. It carries Pu in the reduced state and its behavior is similar to $U(C_2O_4)_2$. The solubility of $UO_2C_2O_4$ has been determined, so that its precipitation can be avoided. The use of $Th(C_2O_4)_2$ in an extraction step is described in the next process.

Thorium Oxalate - Sodium Uranyl Acetate

The $Th(C_2O_4)_2$ - $NaUO_2Ac_3$ process consists of a $Th(C_2O_4)_2$ extraction followed by decontamination and concentration cycles using $NaUO_2Ac_3$. The conditions for extraction with $Th(C_2O_4)_2$ are 0.25 M UO_2(II), 1 M HNO_3, 0.015 M Th(IV), 0.05 M $H_2C_2O_4$. A concentration of Fe(III) as high as 0.05 M does not interfere. This step is coupled with a $NaUO_2Ac_3$ process in any of the following three ways:

The extraction precipitate in the first method is dissolved in excess $(NH_4)_2Ce(NO_3)_6$, which oxidizes Pu when cold. The excess Ce(IV) ion is then destroyed with Cr(III). Sodium uranyl acetate is then precipitated by adding UO_2(II), $NaNO_3$, and NaAc. The advantage of this method is that it can be performed at room temperature.

In the second method the $Th(C_2O_4)_2$ precipitate is dissolved in $Na_2Cr_2O_7$ or $(NH_4)_2Ce(NO_3)_6$ plus $Na_2Cr_2O_7$. The Pu(VI), $Cr_2O_7^{--}$, and Ce(IV) are then reduced with SO_2. The acid concentration is raised to 4 M and $H_2C_2O_4$ added to precipitate $Th(C_2O_4)_2$ again which carries Pu(IV). This precipitate is dissolved with more $(NH_4)_2Ce(NO_3)_6$ which again oxidizes Pu. The Ce(IV) is destroyed with Cr(III). The oxidized Pu is then carried by $NaUO_2Ac_3$ by adding UO_2(II), $NaNO_3$, NaAc. This method gives greater decontamination than the first method because the fission oxalates are more soluble in the higher acid concentrations.

In the third method the $Th(C_2O_4)_2$ is dissolved in $(NH_4)_2C_2O_4$. Thorium oxalate is precipitated again and dissolved in HNO_3. Oxidation is then performed with dichromate plus Ce(III) catalyst to obtain Pu(VI). Then $NaUO_2Ac_3$ is precipitated, dissolved, and reprecipitated. Laboratory tests on this method gave an overall yield of 95% and gamma decontamination of 6×10^5.

Cerous Fluoride

Cerous fluoride seems to be identical to LaF_3 with respect to its physical properties and its ability to carry Pu at W concentrations, but it may have certain advantages over LaF_3. It appears to dissolve in $NaBiO_3$ in 5 N HNO_3, and this procedure, although briefly studied, might make possible a new coupling step to the Hanford process for the fluoride method if Ce(III) is used as carrier. A further possible advantage is that it could be added as Ce(IV) salt to a fluoride solution containing Pu without precipitating and then could be reduced in solution to give a co-formed precipitate.

Cerous fluoride can be used as an alternate for or coupled with LaF_3. In laboratory extraction tests it gives the same yields. Cerium(IV), like Zr(IV), will dissolve PuF_4 plus CeF_3 or LaF_3 at room temperature. Simultaneously, the Ce(IV) oxidizes Pu. Experiments in stainless steel equipment, however, have given erratic results. The addition of a strong oxidizing agent as $NaBiO_3$ might eliminate this difficulty. After oxidation KNO_3 and HF are added to make by-product precipitates of CeF_3 (or LaF_3) and some CeF_4. A molecular ratio for K to Ce(IV) or at least 1:1 appears to be necessary to precipitate completely any remaining Ce(IV). Cerium(III) is quantitatively precipitated by HF even in the absence of K. The oxidized solution can then be reduced with .02 M Fe(II) at room temperature and the cycle repeated for decontamination and concentration.

Lanthanum Oxalate

Plutonium reduced with $NH_2OH \cdot HCl$ is carried by $La_2(C_2O_4)_3$, and yields of over 95% have been obtained in tracer experiments. Lanthanum oxalate is suitable for Cb_2O_5 coupling because Cb and Zr form stable complexes with oxalate ions and should remain in solution when the oxalate precipitates. In the coupling, reduced Pu is extracted from UNH solutions by Cb_2O_5. After washing, the Cb_2O_5 precipitate is slurried by adding $La(NO_3)_3$, HNO_3, and $NH_2OH \cdot HCl$. Then $H_2C_2O_4$ is added and a precipitate of $La_2(C_2O_4)_3$ is formed with La. This precipitate is then washed and dissolved in 16 $\underline{M}$ HNO_3.

Thorium Molybdate

Thorium molybdate, in laboratory tests with 0.1 $\underline{N}$ HNO_3 and about 0.1 mg./cc. of thorium, carried about 99% of tracer Pu. This carrier is useful in separating element 93 of which only 2 or 3% of tracer amounts was carried in the same tests. There may be some advantage in using $Th(MoO_4)_2$ for extracting Pu from UNH solutions, and it might be possible to use it following a different carrier for extraction such as $U(C_2O_4)_2$ or $BiPO_4$.

Bismuth Hydroxide

Bismuth hydroxide carries reduced and oxidized Pu equally and has been considered for various alternate concentration schemes for the Hanford process. The most promising of these was described previously in the section on the Hanford process. Another concentration method consists of neutralizing the acid solution from the $BiPO_4$ by-product precipitation in the concentration cycle. This neutralization precipitates $Bi(OH)_3$ which carries Pu. Less HNO_3 is required for the dissolution of $Bi(OH)_3$ than of $BiPO_4$. The solution can then be oxidized with $NaBiO_3$, and another $BiPO_4$ precipitate and another $Bi(OH)_3$ precipitate made for further volume reduction. A 92% laboratory yield was obtained after two such concentration cycles.

Other Insoluble Metal Hydroxides

The other insoluble metal hydroxides besides Bi that have been tested for the concentration step in the Hanford process are Al, Cu, Ce, Fe(III), La, Ni and Zr. Because oxidized Pu is carried by these hydroxides, a reduction step is unnecessary. The oxidized solution from the $BiPO_4$ by-product precipitate in the Hanford concentration cycle is made alkaline with NaOH or KOH to precipitate the hydroxides. Concentration can be achieved by the exchange of Pu between smaller and smaller amounts of carrier. The hydroxide carriers are soluble in NaOH and NH_4OH and no oxidation-reduction is necessary. One typical process is to precipitate with $Al(OH)_3$, dissolve in NaOH, precipitate with $Cu(OH)_2$, dissolve in NH_4OH, and then repeat with less Al.

Lanthanum Phosphate

Lanthanum phosphate carries Pu in the reduced state, and is another carrier that has been tested for the Hanford concentration process. It can be precipitated from H_3PO_4 - HNO_3 solutions, from which $BiPO_4$ or LaF_3 would normally be precipitated, by adding La(III) and neutralizing about 90% of the HNO_3 with NaOH. In laboratory tracer tests, over 98% Pu was carried. Lanthanum phosphate is quite soluble in HNO_3 acidities of 1 N or higher. Bismuth phosphate could be precipitated to carry the Pu directly from a reduced solution or carriers such as $Th(IO_3)_4$ or UP_2O_6 might be applicable. An oxidation step could be carried out in a HNO_3 solution of $LaPO_4$ and further concentration secured by standard fluoride cycles. Also after oxidation, $LaPO_4$ might be separated as by-product, Pu reduced, and $LaPO_4$ precipitated again to carry Pu.

Other concentration procedures with $LaPO_4$ have been tried in the laboratory. In one of these the $LaPO_4$ precipitate carrying Pu was dissolved in HNO_3, cupferron was added, and the Pu was extracted with chloroform, which was distilled off as a concentration step. Some decomposition of cupferron by HNO_3 occurred in this laboratory test. Another system was to dissolve $LaPO_4$ carrying Pu in a neutral or alkaline solution using a complexing agent, such as tartaric acid, $(CHOHCO_2H)_2$, for La and Pu. This eliminated decomposition of the cupferron by HNO_3 and also complexed any Fe(III) present so that it was not extracted with cupferron. Iron(III) could be present from corrosion or previous reduction with Fe(II).

Only preliminary laboratory tests have been made on the above concentration methods for using $LaPO_4$, and work has been discontinued in favor of the regular Hanford process.

Uranous Hypophosphate

Uranous hypophosphate (UP_2O_6) has also been tested in the laboratory as a carrier for Hanford concentration procedures. It is not filterable, but carries Pu at W concentrations. The presence of Fe interferes to some extent, but this may be due to the oxidation of U(IV). Urea, 0.01 M, has been found to stabilize the HNO_3 to prevent this U(IV) oxidation. A possible concentration procedure is to dissolve the $La(OH)_3$-$Pu(OH)_4$ after metathesis in 3 N HNO_3, make this solution 0.01 M in urea, 0.06 M in $P_2O_6^{4-4}$, and add a solution of U(IV) to precipitate UP_2O_6. This precipitate can be dissolved in warm HNO_3 plus H_2O_2, and then LaF_3 precipitated by adding La(III) and HF. This carrier may be quite useful for concentration, because the rare earth elements are not precipitated by hypophosphate at the normal acidities used for carrying Pu. The solubility of plutonium hypophosphate, PuP_2O_6, has been found to be extremely low even in 10% UNH and 5 N HNO_3. Thus hypophosphate might be a good reagent for precipitating the pure Pu without carrier.

Thorium Hypophosphate

Thorium hypophosphate (ThP_2O_6) would probably behave similarly to the UP_2O_6 just described.

Thorium Iodate

Thorium iodate, $Th(IO_3)_4$, could probably be used similarly to the UP_2O_6 as described above.

Uranous Pyrophosphate and Thorium Pyrophosphate

Only a very brief amount of experimental work has been done with uranous pyrophosphate (UP_2O_7) and thorium pyrophosphate (ThP_2O_7). Both compounds are insoluble in 1 N HNO$_3$ and have been found to carry Pu to an extent which has not been fully determined. One difficulty with ThP$_2$O$_7$ might turn out to be that it is very difficultly soluble even in strong HNO$_3$. This might not be true of UP$_2$O$_7$. Some experiments on the latter indicated it might be promising for Hanford concentration, although it seemed to be greatly affected by the presence of Fe.

Uranous Iodate

Uranous iodate is a crystalline precipitate which carries Pu from 1 N HNO$_3$ or from HCl solutions of BiPO$_4$. In both cases the presence of any Fe inhibits precipitation and reduces carrying of Pu, presumably because of oxidation of U(IV) by Fe(III). It has been found that the presence of urea (NH$_2$CONH$_2$) stabilizes the HNO$_3$ solutions with respect to oxidation of U(IV). Urea concentrations of 0.01 M have been sufficient to stabilize the solution with respect to UP$_2$O$_6$ precipitation, but the use of urea with UI$_4$ has not been tried. This carrier, if sufficiently stable, would be very good for Hanford concentration because it will dissolve rapidly in HNO$_3$ and it is possible that the UI$_4$ could be precipitated again from the resulting solution.

Uranous Phosphate and Uranous Arsenate

A laboratory investigation of uranous phosphate, U$_3$(PO$_4$)$_4$, and uranous arsenate, U$_3$(AsO$_4$)$_4$, showed that neither carried reduced Pu appreciably under the conditions tested. Thus they might have some use in Hanford decontamination if it is not desired to change the oxidation state of Pu.

Ammonium Uranyl Phosphate

Ammonium uranyl phosphate carries oxidized Pu when precipitated from solutions of about 0.5 N HNO$_3$. It is rather crystalline and seems to be readily soluble in stronger HNO$_3$. Since it also partially carries Pu in the reduced state, it probably could not be used in a process similar to NaUO$_2$Ac$_3$. However, it may be of some value for concentration. For example, it could be precipitated from oxidized solutions in connection with the present decontamination process and dissolved in HNO$_3$. Then the Pu could be reduced and LaF$_3$ or some other carrier could be precipitated to carry Pu from the solution.

Bismuth Antimonate and Bismuth Pyroantimonate

Since BiPO$_4$ and BiAsO$_4$ both appear to carry Pu to a very high degree, bismuth antimonate and bismuth pyroantimonate may have definite possibilities for this purpose. Their use, however, has not yet been investigated.

Bismuth Oxalate

Bismuth oxalate carried Pu to the extent of 90-95% in laboratory tests when precipitated in large amounts from 1 N HNO$_3$ solutions. However, since this carrier is extremely insoluble, it does not appear to have any practical usage.

Zirconium Phosphate

Zirconium phosphate carried about 85% of the Pu from a 1 N HNO$_3$ solution. A possible method for high concentration might be precipitating Zr(PO$_4$)$_4$ from 2 N HCl solutions of BiPO$_4$, dissolving in HF, and then precipitating LaF$_3$.

SOLVENT EXTRACTION PROCESSES

In the solvent extraction processes the Pu and a small percentage of fission products are extracted from the U solution by an immiscible solvent and then the Pu is extracted from the solvent by a small volume of aqueous UN solution. This cycle can be repeated for additional decontamination, concentration, and purification.

This section of this report describes an extraction process in which diethyl ether ($C_2H_5OC_2H_5$) is used as solvent. Three couplings of this process to precipitation processes are also included. The use of chloroform ($CHCl_3$) extraction coupled to an adsorption process is described in the next section of this report, "Adsorption Processes". No doubt other solvents satisfactory for solvent extraction of Pu will be found. A complete separation process employing solvent for extraction, decontamination, concentration and isolation of Pu has not been developed.

Ether Extraction

The ether extraction process is based on two experimentally proved facts. The first of these is that equilibrium distribution of Pu in the oxidized state between ether and water solutions of UN is such that quantitative recovery can be effected by countercurrent extraction provided the UN concentration in the aqueous phase is greater than 35%. Ten to fifty-fold decontamination will be effected simultaneously. The second fact is that Pu in the reduced state is extracted quantitatively from ether-UN solutions by a comparatively small volume of aqueous-UN solution. The transfer of by-product into the water under these conditions is 50-100% of that in the ether phase. The ether extraction process as visualized at present, based on completed laboratory and semi-works investigations on tracer scales, is described below. A flowsheet (Figure 2) is attached.

Status: The status of the ether extraction process as of June 1, 1944 is as follows. Fifteen runs in the Chicago semi-works indicate that the ether extraction process is mechanically operable. However, insufficient data at equilibrium conditions have been obtained to permit any definite conclusions to be reached as to the chemical aspects such as yields and decontamination. The above runs were made with about 1/5 to 1/10 of Clinton levels of Pu and by-product concentrations. This process has yet to be evaluated at Clinton and Hanford levels, and several additional experiments will be necessary before a plant design could be made.

Metal Solution: The solution of the U for this process is accomplished by the methods described in a previous section of this report, "Metal Solution". In this case, however, the solution is only diluted to about 45% UN and contains an excess of HNO_3 (about 1 N) which is necessary to prevent the formation of a U compound precipitate in the presence of radiation at W levels. The solution is oxidized using 0.1 M $Na_2Cr_2O_7$ at 85°C. for 2 hours before being jetted to the continuous ether extraction system.

Extraction: The oxidized metal solution is extracted continuously in a countercurrent extraction column with an ether solution of UN. The concentrations of UN in the two phases are in equilibrium (45% and 38% for the aqueous and ether phases respectively), and there is no UN transfer. The maximum amount of Pu is extracted from a 45% UN aqueous solution; increased UN percentage gives no greater yield and with UN below 20-30%, the Pu recovery falls off appreciably. A volume ratio of 3:1 for ether to water seems to be optimum for the ether extraction column. Preliminary countercurrent experiments on a tracer scale indicate that almost all of the Pu and about 1.5-10% of the by-products are transferred from the aqueous to the ether phase. All of the UN which was originally contained in the aqueous phase and 90-98% of the by-products are discharged in the aqueous phase waste.

The ether phase from the first column, which contains practically all of the Pu, is extracted in a second column with a comparatively small volume of aqueous reducing solution containing an equilibrium amount of UN. Tracer scale experiments, now confirmed by semi-works runs show that almost all of the Pu and a large fraction of the fission products contained in the ether phase will transfer completely to the aqueous phase. Hydrazine sulfate, present in 0.1 M concentration, was the best reducing agent of those tried for this step. Preliminary tests indicate that the concentration of Pu in the aqueous solution can be built up indefinitely as long as a sufficient excess of reducing agent is present. The reducing agent, however, in some cases is quickly consumed when only 0.1 M concentration is used.

Decontamination: In semi-works tests gamma decontamination factors of 12-15 and beta decontamination of 40-70 have been obtained in overall cycles through both columns. Two schemes have been proposed for obtaining the additional decontamination which is required in the W canyon. Neither of these proposed methods has been tested experimentally. The first scheme is based on the possibility that the small percentage of by-product which transfers with the product during the initial ether extraction and again in the aqueous extraction operation can be removed by reducing the aqueous solution from the metal dissolver and carrying out a countercurrent continuous extraction in this state. There would be no Pu transfer in the reduced state, and the aqueous discharge could than be oxidized and a regular ether extraction cycle carried out as previously described. The second proposed scheme consists simply of repeating the described cycle of ether and aqueous extractions until the desired decontamination is obtained. It appears that about 6-7 such cycles would be necessary to obtain the 10^{7} gamma decontamination factor which is required at Hanford. Based on semi-works results to date, however, the overall product loss for this number of cycles would probably be excessive.

Concentration: Semi-works tests were operated with a 3-fold concentration but it is possible to use much less aqueous solution in the second column, and concentration factors of 100-fold for each cycle of ether plus aqueous extraction appear feasible. If several such cycles are carried out in order to obtain satisfactory decontamination, similar concentrations will be obtained in each cycle.

Uranium Recovery: The proposed U recovery step in the ether extraction process is carried out by first adding a so-called "selectivity agent" to the aqueous solution from the ether extraction column, which contains all of the dissolved U and at least 90% of the fission products. This agent is capable of displacing the equilibrium distribution of UN between the water and ether phase in favor of the ether phase. The UN is then extracted by countercurrent ether extraction. The ether is purified for recycling by distillation or by water extraction of UN as shown in the attached flowsheet, Figure 3. The extracted UN is recovered in either case as an aqueous solution substantially free of by-products. It is desirable, but not necessary, that the selectivity agent be capable of recovery and recycling. It has been shown(A-1022) that several salts including $NaNO_3$, KNO_3, and $Ca(NO_3)_2 \cdot 4\ H_2O$ have the desired effect on the equilibrium distribution of UN between phases. It is hoped, however, to find a volatile selectivity agent which can be recovered by distillation.

Waste Disposal: The active aqueous waste solutions are disposed of in a similar manner to that employed in the present Hanford process. The possibility exists, however, that the aqueous solution of fission products, stripped of U, can be concentrated and used for other purposes.

Yields: Erratic yields were obtained on the 15 semi-works runs that have been made. However, yields of 98-99% are indicated for each cycle of ether plus aqueous extraction when optimum conditions are established.

Explosion Hazards: A potential hazard exists in the handling of diethyl ether, because of the inflammability of ether and because of the possible formation of explosive ether peroxides. In addition, there is some evidence that UN crystals formed under certain conditions and ether solutions of UN might be explosive. After an investigation of this subject, including detonation tests, it was concluded that explosion and fire hazards can be minimized by proper precautions and that the peroxide concentration will not build up sufficiently to be dangerous. In operation of the semi-works equipment, the relative humidity of the room is maintained greater than 75% so that in the event of ether leakage, explosive mixtures will not be formed. As a further precaution, the solutions and residues are tested periodically for sensitivity to mechanical shock. Operation of ether extraction units by the Mallinckrodt Company and at the Chicago semi-works for some time without accident show that ether extraction systems can be designed for safe operation.

Oxidizing and Reducing Agents: The present oxidizing agent for the metal solution for this process is 0.1 M $Na_2Cr_2O_7$, and this has been used successfully in the semi-works.

The present reducing agent for the aqueous solution in the second column is 0.1 M hydrazine sulfate. Other reducing agents, 0.05 M $U(SO_4)_2$ and 0.05 M $NH_2OH \cdot H_2SO_4$, tried previously, proved to be unsatisfactory.

Advantages and Disadvantages: The mechanical advantages for the ether extraction process are as follows:

1. A continuous process such as this one is more subject to reproducible operation and to remote control than a batch process.

2. The equipment required is of small size and simple design.

3. The volumes of waste and process solutions are small.

4. It is not necessary to handle any active solids such as precipitates.

The chemical advantages are as follows:

1. There are no chemical or physical conditions which must be maintained within very narrow limits, as is the case in the precipitation processes.

2. The quantity and number of chemicals required are small.

3. Uranium, substantially free of fission products, can be recovered as an integral part of the process.

4. The possibility also exists that fission product concentrates can be recovered if desired.

The mechanical disadvantages are:

1. The successful operation of a continuous process depends upon the simultaneous functioning of all parts of the system.

2. The formation of emulsions caused by the presence of oil or other impurities in the system might make continuous countercurrent extraction difficult.

The chemical disadvantages are:

1. There is a potential fire and explosion hazard in a process handling large quantities of ether and ether solutions of UN.

2. Radiation at W levels might have an undesirable effect on the UN-ether-water system which will limit the allowable time of phase contact in the extraction columns and might, therefore, limit the efficiency of the process.

Ether Extraction - Bismuth Phosphate

A coupling of ether extraction to the $BiPO_4$ process has been tested in the laboratory. In this process the reduced aqueous product solution from the ether extraction cycle is diluted to 20% UNH and made 1 N in H_2SO_4. A regular $BiPO_4$ process then follows starting with a Pu precipitate. In a laboratory test a 97.5% yield was obtained on the first $BiPO_4$ precipitate, and the overall yield for this precipitate plus one decontamination cycle (two precipitations) was 91.5%. These figures do not include the ether extraction cycle yield.

Ether Extraction - Lanthanum Fluoride

In a coupling of ether extraction to the LaF_3 process, the aqueous solution containing reduced Pu from the ether extraction cycle is diluted to 20% UNH and made 1 N in HNO_3. Lanthanum fluoride is then precipitated to carry Pu and then a regular LaF_3 process is carried out. Very little work has been done on this combination process.

Ether Extraction - Sodium Uranyl Acetate

In a coupling of ether extraction to a $NaUO_2Ac_3$ process, the reduced Pu solution from the ether extraction cycle would be diluted to about 1-2% UNH, adjusted to 0.4 N in HNO_3, and heated for 1 hour at 75°C. with a 0.1 N $Na_2Cr_2O_7$ concentration to oxidize the Pu. Sodium acetate and $NaNO_3$ would then be added to precipitate the Pu with $NaUO_2Ac_3$ and a standard $NaUO_2Ac_3$ process follows. There is some experimental evidence that the most important fission product remaining with Pu in the ether extraction process is Ru. This element is not carried by $NaUO_2Ac_3$, and a very good decontamination should be obtained using this combination process. This coupling has not been tested in the laboratory.

ADSORPTION PROCESSES

In the adsorption processes the reduced metal solution (40% UNH) is diluted to 10% UNH and passed through a column containing a synthetic ion exchange resin which adsorbs all of the Pu and small amounts of U and fission products. These elements are then elutriated from the column selectively by a series of washes. Subsequent adsorption cycles can be performed on the Pu wash for additional decontamination, concentration, and isolation. An all-adsorption process for preparation of Pu with satisfactory purity has not yet been perfected. The following review includes descriptions of all-adsorption processes and also couplings of adsorption extraction to wet precipitation processes. Most of the data in this review were taken from reports CN-1431, CN-1442, and CN-1443, which should be consulted for further details.

Adsorption Extraction

All of the adsorption processes are based on a preliminary U extraction step in a column containing Amberlite IR-1, an ion exchange synthetic resin, manufactured by the Resinous Products and Chemical Company. Considerable laboratory work has been done in developing this adsorption extraction step and a discussion of the variables involved follows.

Status: The status of development work on the adsorption extraction step as of June 1, 1944 may be summarized as follows: All of the adsorption tests to date have been performed only in the laboratory, but some of the mechanical operations have been checked in the semi-works. A detailed study shows that the adsorption extraction step is chemically and mechanically feasible and should be operable on a plant scale. Adsorption extraction equipment for installation in Cell No. 2 of the Clinton plant has been designed but no action has been taken for its construction and installation (CN-1431).

Knowledge of adsorption extraction step is complete except that a more detailed study of impurity effects on product adsorption, and also the effects of rate of flow, solution concentration, and column geometry in the elutriation steps should be carried out. Laboratory tests have shown a deviation in results between runs made in stainless steel and glass columns. Additional investigation of the exact nature of the cause of this deviation is necessary, as well as a study of methods for its elimination. Essentially all of the adsorption studies have been carried out with tracer concentrations of Pu. Although batch tests have shown that adsorption equilibria remain constant up to Hanford product concentrations, column experiments should be carried out as soon as possible to check cycle operation at these higher concentration levels.

Principle: The principle of adsorption extraction is that ion exchanges take place between the uranyl and other metallic ions in the UNH solution and the replaceable ions in the Amberlite IR-1 resin. The exchange reactions in general are reversible and are visualized as follows when the solutions are passed successively through an Amberlite IR-1 resin bed.

1. Adsorption: UNH solution

$$2\ NaR + UO_2^{++} \rightleftharpoons UO_2R_2 + 2\ Na^+$$

$$2\ UO_2R_2 + Pu^{+4} \rightleftharpoons PuR_4 + 2\ UO_2^{++}$$

$$\frac{n}{2}\ UO_2R_2 + M^{+n} \rightleftharpoons MR_n + \frac{n}{2}\ UO_2^{++}$$

where R = parent body of resin
M = any by-product cation
n = valence of adsorbed cation

2. Uranium desorption: H_2SO_4 wash

$$UO_2R_2 + 2\ H^+ \rightleftharpoons 2\ HR + UO_2^{++}$$

3. Product and by-product desorption: $NaHSO_4$, $H_2C_2O_4$, H_3PO_4

$$PuR_4 + \begin{pmatrix} 4\ H^+ \rightleftharpoons 4\ HR \\ 4\ Na^+ \rightleftharpoons 4\ NaR \end{pmatrix} + Pu^{+4}$$

$$MR_n + \begin{pmatrix} nH^+ \rightleftharpoons nHR \\ nNa^+ \rightleftharpoons nNaR \end{pmatrix} + M^{+n}$$

The above equations indicate that by-product cations are adsorbed and desorbed together with the Pu. However, as will be discussed later under adsorption extraction method No. 2, it is possible to elutriate the Pu selectively so that very little by-product is associated with it.

Extraction Methods: The adsorption extraction methods which have been considered may be summarized as follows:

TABLE IV

Summary of Adsorption Extraction Methods

Extraction Method	Uranium Wash	By-product Wash #1	Product Elutriant	By-product Wash #2
1.	2.5% H_2SO_4	None	18% $NaHSO_4$	None
2.	2.5% H_2SO_4	0.75% $H_2C_2O_4$	5% $H_2C_2O_4$	18% $NaHSO_4$
3.	2.5% H_2SO_4	10% H_3PO_4	18% $NaHSO_4$	None
4.	2.5% H_2SO_4	10% H_3PO_4	5% $H_2C_2O_4$	18% $NaHSO_4$
5.	2.5% H_2SO_4	0.75% $H_2C_2O_4$	5% $H_2C_2O_4$	None

In extraction method No. 1 (Figure 3) a reduced 10% UNH metal solution from the dissolver is passed through the Amberlite IR-1 resin bed and essentially 100% Pu, 14% U, 90.5% beta and 89.1% gamma are adsorbed. All the U is then elutriated by 2.5% H_2SO_4. Next, the Pu is desorbed with an 18% $NaHSO_4$ solution which removes 97.7% of the Pu plus 75.7% beta and 51.7% gamma. The column is then backwashed with water which removes an additional 2.3% Pu, .4% beta and .8% gamma. The Pu in this waste solution might be recovered by recycling. There is also a final water rinse as shown. It should be noted that this flowsheet leaves about 11.7% beta and 34.1% gamma activity in the column for each batch. This activity buildup will be discussed later under resin waste disposal. This flowsheet gives a 97.7% Pu yield and decontamination factors of 1.5 for beta and 2.2 for gamma.

In extraction method No. 2 (Figure 4) a reduced 10% UNH solution is passed through the Amberlite IR-1 resin and essentially 100% Pu, 14% U, 89.9% beta and 90.9% gamma are adsorbed. All of the U is elutriated by 2.5% H_2SO_4. Next, 0.75% $H_2C_2O_4$ is passed through to elutriate 13.2% beta, 42.3% gamma, and 1.9% Pu. About 95.4% of the Pu is elutriated with 5% $H_2C_2O_4$. This Pu solution contains only 1.0% of the beta and 1.5% of the gamma activity that was in the original UNH solution. The second by-product wash removes 68% beta and 41.1% gamma plus 2.7% Pu. This leaves the column with about 3% beta and essentially no gamma activity. The Pu loss in the first by-product wash appears irreducible except by further research in the use of lower concentrations of $H_2C_2O_4$. The second wash with its Pu loss will probably be eliminated if further research shows that it can be done without decreasing decontamination factors, because its purpose is merely to remove the column by-product activity between adsorption cycles. This flowsheet gives a 95.4% product yield, and decontamination factors of 100 for beta and 67 for gamma. The present Hanford precipitation process has an extraction step decontamination factor of about 12. Extraction method No, 2 seems to be definitely more attractive than extraction method No. 1 because it results in an additional 30-fold gamma decontamination factor. Extraction method No. 2, however, has not been tested as completely as extraction method No. 1 and requires additional reproducibility studies for complete verification.

Extraction method No. 3 (Table IV) has been tested in the laboratory as a special extraction step coupled to a titanium zeolite adsorption decontamination cycle which is described later. Preferential desorption of practically all of the adsorbed Zr and Cb is obtained with 10% H_3PO_4 and this is of importance in this coupling because these fission elements are not decontaminated very well by titanium zeolite.

Extraction method No. 4 (Table IV) is a hypothetical substitute for extraction method No. 2 for efficiently removing Zr and Cb from the column. However, extraction method No.2 results in higher La decontamination than extraction method No. 4.

Extraction method No. 5 (Table IV) is a proposed modification of extraction method No. 2 in which the second by-product is eliminated to save cycling time, waste disposal volume and Pu loss. A reproducibility series would have to be made on extraction method No. 5 to certify that no decrease in decontamination factor is obtained throughout successive cycles.

Bed Materials: Although Amberlite IR-1 resin has been adopted as the most promising resin for the extraction column and the adsorption processes have been developed with it, extraction of Pu by adsorption methods can be carried out with many types of adsorbent materials. Table V gives a list of those tried with the corresponding laboratory test results. Titanium zeolite and Amberlite IR-4 have been considered for a second or decontamination column and these couplings are described later. It is desirable that the resin in the second column for such coupling processes adsorb the Pu and practically no by-product. It is believed that several new types of ion exchange resins could be prepared to be more specific in their adsorption of the Pu than any types commercially available at present. Offers have been made by the resin manufacturing companies to cooperate in preparing such adsorbents to be submitted for testing to the Metallurgical Laboratory, but pending further decisions, no work is being carried out along these lines.

Column Variables: The data from laboratory experiments on the adsorption columns for the extraction of Pu by Amberlite IR-1 have been correlated using a "storage capacity", $H_s(1-F)$, and a "mass transfer rate", K, obtained in a manner analogous to the procedure for determining heat transfer constants in a bed of broken solids developed by T. E. Schumann and C. C. Furnas (CN-1443). These correlations apply to down-flow of UNH solutions in glass columns (0.8-6.0 cm.dia.). From the data obtained in these experiments it was found that the transfer rate

1) Increased with increasing UNH flow rate
2) Increased with increasing mesh size
3) Decreased with increasing pH.

Also it was found that the storage capacity

1) Increased with increasing mesh size
2) Increased with increasing pH
3) Decreased with increasing UNH concentration
4) Decreased with increasing temperature.

Due to shrinkage in resin volume on adsorption and to the difference in adhesion of resin to the stainless steel and glass surfaces the performance in stainless steel columns on a laboratory scale (up to 6 in. dia.) does not check operation in glass. It has been recommended that a factor of 0.5 be applied to plant stainless steel design values based on glass columns. On the basis of these correlations the 2'-6" dia. x 5' high stainless steel column using 50-70 mesh IR-1 resin (dry analysis) which has been recommended for a plant process (CE-1431) has a safety factor of 15% based on a free cross sectional area and operating at 25°C. and 1% breakthrough of Pu. This safety factor, however, will very nearly disappear if the temperature rises to 35°C.

The effect of column variables can be shown more directly if the correlation is used to calculate values of "extraction capacity", E, for a chosen adsorption system and then show how each variable affects E (CN-1442). The exchange capacity, E, can be defined as the number of micrograms of Pu adsorbed per cc. of Amberlite IR-1 in a column bed up to the point where an instantaneous breakthrough concentration of 5% of the entering Pu concentration is obtained. Breakthrough is defined as the leakage of Pu through the adsorbent bed.

TABLE V

Laboratory Test Results on Adsorption Bed Materials

No.	Name	Description	Laboratory Test Results
1.	Bentonite		Slow adsorption rate for Pu.
2.	Silica gel.	Hyporsil, Infilco Co. and also Darian Chemical Corporation.	Must use solution with pH 2.4. Can not be highly acid. Slow column adsorption rate so batch use preferred. Erratic results on yields 28-98%, decontamination factor 22, volume reduction 64.
3.	Activated charcoal		Low adsorption capacity for Pu.
4.	Fuller's Earth		Poor overall separation. Also adsorbs U.
5.	Decalso		Non-uniform properties.
6.	Alumina		Low adsorption capacity for Pu.
7.	Zeo-carb H	Sulfonated coke	Stable in 2 M HNO_3 up to 75°C. Might use with $Zr_3(PO_4)_4$ which has greater decontamination. Good at low flow rates. Has 60% of IR-1 product adsorption capacity. Non-uniform properties.
8.	Amberlite IR-1	Tannic acid condensation of phenol formaldehyde, then treated with H_2SO_4.	This resin adopted for use in adsorption processes.
9.	Amberlite IR-100	Phenol formaldehyde resin plus sulfonic acid groups.	Slower product adsorption rate than IR-1. Same Pu adsorption capacity and more stable than IR-1.
10.	Titanium zirconium phosphate		Developed to follow Amberlite IR-1. Poor overall separation. Did not find a selective product elutriant.

TABLE V (cont.)

No.	Name	Description	Laboratory Test Results
11.	Zirconium phosphate		Supported on glass wool or beads; fuse on at 400°C. Dissolves off glass in use, so must replace. Glass wool mats badly and hard to renew. Could use glass beads and flush out of column. Good Pu adsorption. Poor overall separation if used with UNH. Poor decontamination with $NaHSO_4$ elutriant from IR-1. Titanium-zirconium phosphate better, titanium zeolite best for second column after IR-1.
12.	Bismuth phosphate		Soluble in HNO_3. Some decontamination.
13.	Lanthanum fluoride	On silica gel.	Product elutriation not satisfactory.
14.	Barium iodate		Poor Pu elutriation with 5 M H_2SO_4.
15.	Titania C		Elutriation not tested.
16.	Alarco A		Elutriation not tested.
17.	GRS-440-52		Elutriation not tested.
18.	GRS-444-75		Elutriation not tested.
19.	R-SA		Low adsorption capacity for Pu.
20.	R-PH_2		Low adsorption capacity for Pu.
21.	Amine Resin		Low adsorption capacity for Pu.
22.	Catex 284		Low adsorption capacity for Pu on second cycle. Poor stability in acid.
23.	Dupont Basic Resins		Soluble in acid.
24.	Uranous fluoride		Low Pu adsorption capacity and dissolves in 10% UNH.

TABLE V (cont.)

No.	Name	Description	Laboratory Test Results
25.	Potassium-thorium fluoride		Low Pu adsorption capacity and dissolves in 10% UNH.
26.	Thorium fluoride	On silica gel.	Low Pu adsorption capacity.
27.	Thorium phosphate	On silica gel.	Low Pu adsorption capacity.
28.	Santocel		Low Pu adsorption capacity.
29.	Silex		Low Pu adsorption capacity.
30.	GRS-444-63		Low Pu adsorption capacity.
31.	Aluminum oxide		Low Pu adsorption capacity.
32.	Bauxite		Low Pu adsorption capacity.
33.	Basic Resin BR		Low Pu adsorption capacity.
34.	Ferrous hydroxide	(CN-508)	Non-selective for Pu on adsorption or elutriation.
35.	Titania hydrates		Used following IR-1, poor decontamination.
36.	Titanium and zirconium hydrates	Made by J. H. Peterson	High gamma adsorption capacity. Did not study elutriation.
37.	Titanium gels.		High Pu and by-product adsorption capacity.
38.	Alkalex	(CN-991) Carbonaceous cation exchanger prepared by treating lignite with NaOH.	High Pu and by-product adsorption capacity.
39.	RP zeolite	(CN-991) Synthetic hydrated sodium aluminum silicates	Unstable in acid elutriants.

TABLE V (cont.)

No.	Name	Description	Laboratory Test Results
40.	Titanium zeolite #1	95% TiO_2 plus 5% C	High Pu and by-product adsorption capacity.
41.	Titanium zeolite #2	95% TiO_2 plus 5% mica	Does not remove Cb plus Zr, so must use IR-1 first. Adsorbs Pu and almost no beta.
42.	Phosphate derivatives of Amberlite IR-4	Prepared by treating resin with mono- and disodium-phosphate as well as with ortho-phosphoric acid.	Clogged column by forming large precipitate $(UO_2)_3(PO_4)_2$.
43.	Phthalic acid.derivatives with COOH exchange groups.	CN-1373	Poor decontamination.
44.	Phenol formaldehyde resin with sulfonic acid exchange groups.	CN-1373	Poor decontamination.
45.	K salt of IR-1 instead of Na salt	CN-1227	Same yield but less decontamination than regular IR-1 (sodium).
46.	Amberlite IR-4		Use following IR-1.

Although any set of column conditions might be chosen as a reference point, the following system has been selected for this description of exchange capacity.

Mesh size (IR-1), 60-100
Bed area, 1 sq. cm.
Bed height, 60 cm.
UNH conc., 10%
Pu conc., 50 μg./liter (tracer)

pH of UNH, 2.4
Temperature, 23°C.
Flow rate, .1 cc./(sq.cm.)(sec.)
or 90 gal./(sq.ft.)(hr.)
Exchange capacity $E = 1.08\ \mu g$ Pu/cc. of bed at 5% breakthrough

The exchange capacity for an IR-1 resin adsorption column

1) Increases with increasing mesh size. $E = .011\ M + .20$
2) Increases with increasing pH. $E = .39\ pH + .26$
3) Increases with increasing product conc. (μg/liter) $E = .0022C$
4) Decreases with U conc. (weight %) $E = 2.02 - .104\ U$
5) Decreases with increasing temperature °C. $E = 1.48 - .017\ T$
6) Decreases slightly with increasing fission product conc.
7) Is unaffected by bed height. $E = 1.08$
8) Is unaffected by bed diameter. $E = 1.08$
9) Is unaffected by UNH flow rate. $E = 1.08$

Elutriants: In the desorption or elutriation step of adsorption extraction it is desirable to remove each adsorbed ion completely in a highly selective manner with the smallest possible volume of elutriant. The variables involved in accomplishing these objectives are:

1) The nature or composition of the elutriant.
2) Its concentration.
3) Its flow rate.
4) Its direction of flow.
5) Its temperature.
6) The column geometry.

Several elutriants have been studied for use with Amberlite IR-1 and a review of their status is shown in Table VI; however, the fundamentals of the elutriating steps are not as well known as those of the adsorption step.

Complexing Agents: For adsorption extraction various complexing agents have been added to the UNH solution to decrease the adsorption of Cb and Zr for greater decontamination. Tannic acid (2.5% in UNH solution) gave 93% Pu, 8% gamma and 50% beta adsorption on Catex 284 in column tests. The use of tannic acid resulted in reduced adsorption of Cb and Zr but was discontinued due to the fact that it is expensive and also complicates Pu analysis. Tannic acid was not tried with Amberlite IR-1. Citric acid (2.5%) in UNH) reduced the adsorption of Cb and Zr and also Pu, but after 6 batches the Pu adsorption dropped rapidly. For this reason the use of citric acid with Amberlite IR-1 was discontinued. Concentrations of citric acid as high as 20% were tried previously with Catex 284 and the amount of Pu adsorbed in one cycle was not decreased. Successive cycles were not studied. Catex 284, however, was discontinued because of lower Pu adsorption on the second cycle without citric acid. Since sodium citrate is more stable than citric acid, it was also tried

TABLE VI

Status of Elutriants for Adsorption (IR-1) Extraction Cycle

Elements to be elutriated	Elutriants	Flow Rate gal./(sq.ft.)(hr.)	Remarks
U	0.25 M H_2SO_4	20-100	Good elutriation for U only.
Pu	1.25 M $NaHSO_4$	17-153	Very little selectivity.
	5% $H_2C_2O_4$	30	Highly selective for Pu, if Zr and Cb removed first.
	1.5 M H_2SO_4		Pu elutriation incomplete with no volume reduction.
	2 M HNO_3		Starts decomposition of resin at room temperature.
	3 M HCl		Too corrosive.
	0.25 M H_2SO_4 and 0.62 or 1.25 M Na_2SO_4		Similar to $NaHSO_4$.
Fission Products	1 M H_3PO_4	30	Highly selective for Zr and Cb desorption. Might form insoluble phosphates.
	0.75% $H_2C_2O_4$		Highly selective for Cb and Zr desorption.
	1.25 M $NaHSO_4$	60	Highly efficient for removing La, Ce and Sr after Pu elutriation by 5% $H_2C_2O_4$
	1 M sodium acetate and 1 M acetic acid		Removes 30% beta but no gamma.

[redacted]

for complexing the fission products. Batch tests with 0.5% sodium citrate in UNH gave the same gamma decontamination as 2.5% citric acid. In column tests it caused a low adsorption of product on the first cycle.

Effect of Impurities: The effect of impurities on adsorption by IR-1 resin has also been studied in the laboratory. Excess formic acid up to 1 M concentration gives slightly greater product and by-product adsorption. Excess HNO_3 up to 0.5 N gives greater adsorption capacity and a greater adsorption rate but might decrease the stability of the resin by nitration. Iron(III) and also Al(III) in concentrations up to 10^{-3} M have no effect on the rate or capacity of Pu adsorption. The effect of excess Hg was not checked. Inactive fission products had little effect on the rate of Pu adsorption.

Temperature: An increase in temperature gives a rapid decrease in the Pu adsorption capacity of IR-1 resin. For this reason it is desirable to keep the resin at or below 30°C. If necessary, refrigerated dilution water could be used to make the 10% UNH. There is approximately a 1°C. rise in the Amberlite IR-1 during adsorption if there is no fission product buildup, such as with adsorption extraction method No. 2. In any event, the temperature of the resin must be kept below 90°C. to prevent its decomposition.

Feed Solution: The clarity, oxidation state, and concentration of the UNH feed solution influences the amount of Pu adsorbed by IR-1 resin. With unfiltered UNH the Pu adsorption was less in laboratory tests, but the added expense and difficulty of filtration are not considered justified for plant operation. A greater amount of Pu is adsorbed from a feed solution in the reduced state than one in the oxidized state. The adsorption extraction process is designed for use of a 10% UNH feed solution. A comparison of 5, 10 and 20% UNH feed solutions shows that a 10% UNH concentration is optimum (CN-1442).

Radiation: To study the effect of radiation on Amberlite IR-1, this resin was exposed to beta or electron radiation while in contact with various solutions in the laboratory. These tests show that this resin is unaffected by H_2O, 3 N HCl, 0.5 N H_2SO_4, 10% UNH, 2 N HNO_3 and 2 N $NaNO_3$ at about 25 times W levels of beta radiation. Because betas and gammas act essentially in the same way, only beta radiation was studied, as a matter of convenience. On the assumption that these results can be extrapolated to W plant conditions of total radiation of beta and gamma, it appears that any of the above solutions could be used without any decomposition of the IR-1. If the resin column were used for a sufficient period to allow buildup of activity or if a solution containing NO_3^- ion were allowed to remain stagnant due to interrupted flow, then decomposition of the resin might result. The flow rates of NO_3^- solutions should be greater than 2-3 cc./(sq.cm.)(min.) or 30-45 gal./(sq.ft.)(hr.) for safety. The activity buildup in the resin column can be minimized by selective elutriation of this activity according to methods described previously (adsorption extraction method No.2).

Waste Disposal: It is expected that the resin will need to be replaced periodically because of activity buildup or operating results such as loss of Pu or increased pressure drop. When replacement of the resin is necessary, it will be removed from the column as a resin-water slurry by means of an air lift and delivered to a tank where it will be dissolved in 3 N HNO_3. This solution will be subsequently neutralized and sent to fission product waste storage. In using extraction method No. 1, approximately 12% beta and

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34% gamma activity from each batch are permanently retained by the IR-1 resin. With extraction method No. 2, only 3% beta and essentially no gamma are retained. Although a series of 21 reproducibility cycles (extraction method No. 1) has been carried out in the laboratory at low activity levels without any progressively deleterious effects on Amberlite IR-1, it is arbitrarily felt that not more than 30 cycles of plant operation at Clinton levels should be definitely expected without replacing the resin bed.

Waste disposal volumes for the adsorption extraction step are compared to the Hanford process extraction step in Table VII which is based on one ton of metal.

TABLE VII

Unneutralized Adsorption (IR-1) Extraction Waste Volumes

Type of Extraction Method	Uranium Storage gal.	By-product Storage gal.	Retention Pond gal.	Total gal.
Adsorption Extraction Method No. 1	8600	1000	2510	12110
Adsorption Extraction Method No. 2	8700	5355	3510	17565
Hanford Extraction	2420	-----	-----	2420

The large quantities of U waste in the adsorption extraction step result from the use of 10% UNH and the necessity of using a H_2SO_4 wash. Consequently, if the adsorption extraction step were substituted for the Hanford process extraction step it would be necessary to provide additional waste disposal capacity for U waste. Little can be said regarding the fission product waste until the coupling and decontamination cycles are more thoroughly developed. Additional storage capacity would be required for these also.

Uranium Recovery: Because approximately the first 30% of the waste UNH feed solution from the adsorption column contains no gamma activity, it is possible by this procedure to recover this portion of the U free of gamma activity. The remaining waste feed solution with the gamma activity could probably be decontaminated by one or more additional resin columns.

Volume Reduction: The volume reduction expected from adsorption extraction based on a 10% UNH solution is 4.2:1. The solution of Pu from one ton of U will have a volume of 121 gal. after adsorption extraction. In the Hanford precipitation process the volume of Pu solution after the extraction step is only 300 gal. However, for the first by-product precipitation this latter solution is diluted to 2690 gal. In a coupling to the Hanford process the adsorption extraction Pu solution would require less dilution but this would be no advantage. Couplings to other processes would probably be similar. This adsorption extraction volume reduction would be advantageous, however, either in an all-adsorption process or in a coupling to a solvent extraction process.

Stainless Steel Columns: With Amberlite IR-1 resin in stainless steel columns an earlier breakthrough of both U and Pu occurs than in glass columns, to the extent that the breakthrough capacity of the stainless steel column is

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approximately 40-60% of the glass column capacity. The cause of this phenomenon has been tentatively attributed to a wall effect of a physical nature. During adsorption the resin contracts and apparently shrinks away from a metal wall, but not from a glass wall. The annular space produced between the bed and the column wall permits some of the feed solution to by-pass the bed. Up-flow passage of the feed corrects this deficiency but is not practical in plant operation. The effect is still present in stainless steel columns as large as 6 in. in diameter. Although it is suspected that this action of the resin bed may not take place in the plant column as large as 2 ft. in diameter, it has been felt necessary to use the laboratory stainless steel column data for design since glass column performance can not be guaranteed. If this effect can be eliminated, it will be possible to use a smaller adsorption bed and smaller amounts of elutriating agents for greater volume reduction.

Corrosion Resistance: The corrosion resistance of 25-12 stainless steel equipment to several of the adsorption process solutions has been tested by the Semi-works Section of the Clinton Separation Development Division. These tests were conducted by refluxing welded test coupons separately in synthetic process solutions for four 48-hour periods each at 40°C. Although these tests did not investigate the sequence of operations in an actual adsorption cycle with respect to activation or passivation, the following data show that these process solutions do not appreciably corrode 25-12 stainless steel.

TABLE VIII

Corrosion of 25-12 Stainless Steel
in Adsorption (IR-1) Process Solutions

Test Solutions	Upper Limit of Corrosion Rate in./mo.
1. 2.45% H_2SO_4; 97.55% H_2O	0.00008
2. 2.11% H_2SO_4; 20.0% $UO_2SO_4 \cdot 3 H_2O$; 77.89% H_2O	0.00009
3. 0.75% $H_2C_2O_4$; 99.25% H_2O	0.00003
4. 5.0% $H_2C_2O_4$; 95.0% H_2O	0.00005

Advantages and Disadvantages: The advantages of adsorption extraction are:

1. The equipment is simple and readily available.
2. Most of the Cb and Zr are removed. (Extraction method No. 2).
3. About 30% of the U can be recovered free of gamma activity.
4. A solution of fission products high in gamma activity can be isolated.
5. There is high decontamination by adsorption extraction method No.2; 100 for beta and 67 for gamma compared to 28 and 12 respectively for the Hanford precipitation extraction.

The disadvantages of adsorption extraction are:

1. Radiation on the resin for long periods of time at W levels may be detrimental.
2. There are large volumes of waste solutions.

Couplings: The adsorption extraction step, of course, needs to be coupled either to wet precipitation processes or to additional adsorption steps for a complete separation process. Because coupling to the Hanford process results in a poor overall decontamination, a preliminary survey has been made of couplings to various other precipitation processes. The various couplings are described in the next section. It should be emphasized that in general they are only in initial states of development. A comparison of yield and decontamination data on the more important couplings is shown in Table X. A number of couplings to the adsorption extraction method No. 2 appear promising but need further tests for verification.

An all-adsorption process, if it can be perfected, possesses the following advantages:

1. The mechanical operations of centrifugation, filtration, precipitation, agitation, dissolving, heating and cooling would be eliminated, making a process which is more easily adapted to methods of remote control.
2. The chemical operations of oxidation, reduction and metathesis would be eliminated.
3. Because of the volume reduction inherent in adsorption cycle operations, smaller sized equipment and smaller quantities of chemicals throughout successive cycles would be required.
4. The successive use of various adsorbents, highly specific for different fission elements, might reduce the number of steps necessary to produce the required decontamination.

Adsorption (IR-1) - Bismuth Phosphate

The direct substitution of adsorption extraction method No. 1 for the extraction step of the $BiPO_4$ process is chemically satisfactory with respect to Pu yield, although the normal H_3PO_4 concentration of 0.1 M must be increased to at least 0.4 M in the by-product precipitation coupling step. The overall gamma decontamination effected by adsorption extraction method No.1 plus one $BiPO_4$ decontamination cycle is much lower, however, than that secured through the first decontamination cycle of the regular Hanford process, primarily because of the low decontamination in the adsorption extraction. For this reason this coupling should not be considered for plant operation.

The coupling of adsorption extraction method No. 1 to the $BiPO_4$ process as an additional step rather than as a substitution for extraction also is satisfactory with respect to yield and chemical feasibility, and requires no modification of the present process procedure. Although this coupling, adsorption extraction plus one $BiPO_4$ precipitation, gives an overall gamma decontamination about equal to the $BiPO_4$ process extraction, there seems to be no advantage in using it, because of the extra step of adsorption.

A direct coupling of adsorption extraction method No. 2 to the $BiPO_4$ process involves the necessity of destroying the large amount of $H_2C_2O_4$ in the

Pu solution by oxidation with $KMnO_4$. As carried out, the partially oxidized Pu must also be reduced with H_2O_2 before the $BiPO_4$ product precipitation. No gamma decontamination factors for the overall process are available since too low an activity level prevailed in all laboratory tests to permit measurement. The beta decontamination factors are in excess of 10^4. The chemical and mechanical problems involved in the destruction of large amounts of $H_2C_2O_4$ make this process unattractive. A more simple means of separating the Pu from the large excess of $H_2C_2O_4$ is to make a $U(C_2O_4)_2$ precipitate before coupling to the $BiPO_4$ process.

From the above discussion it can be seen that direct couplings of adsorption (IR-1) extraction to the $BiPO_4$ process do not appear promising.

Adsorption (IR-1) - Sodium Uranyl Acetate

The coupling of adsorption extraction method No. 1 to a modified $NaUO_2Ac_3$ cycle (product plus by-product precipitation) is satisfactory for yield and chemical feasibility. Considerable laboratory work has been done on this coupling; however, the high decontamination of the first precipitation is not repeated with the second. A cross-over to the $BiPO_4$ process as described in the next coupling seems more promising.

Adsorption (IR-1) - Sodium Uranyl Acetate - Bismuth Phosphate

The indirect coupling of adsorption extraction method No. 1 to the $BiPO_4$ process through a $NaUO_2Ac_3$ product precipitation produces an overall decontamination in excess of 10^4 through one precipitation. In the limited number of runs made, however, an unsatisfactory Pu yield has been obtained upon throwing down the $BiPO_4$ product precipitate from the H_2SO_4 solution of the $NaUO_2Ac_3$ precipitate. Additional work on this cross-over is necessary.

Adsorption (IR-1) - Uranous Oxalate - Sodium Uranyl Acetate - Bismuth Phosphate

The indirect coupling of adsorption extraction method No. 2 to the $BiPO_4$ process through $U(C_2O_4)_2$ and $NaUO_2Ac_3$ product precipitations has produced overall decontamination factors in excess of 10^5 through the $NaUO_2Ac_3$ step. Activity levels were too low to carry the process any further in the laboratory. Plutonium yields in the $U(C_2O_4)_2$ precipitation have been extremely poor (less than 80%) and have been complicated by analytical difficulties in the laboratory. Increased digestion time has recently resulted in higher Pu yields but additional investigation is still in progress. This coupling at present seems to be the most promising of those tried.

Adsorption (IR-1) - Uranous Oxalate - Bismuth Phosphate

Adsorption extraction method No. 2 can be coupled to the $BiPO_4$ process through an intermediate $U(C_2O_4)_2$ precipitation. This coupling is presumably subject to the same analytical difficulties encountered in the coupling described previously.

Adsorption (IR-1) - Uranous Oxalate - Sodium Uranyl Acetate

Adsorption extraction method No. 2 can also be coupled through an intermediate $U(C_2O_4)_2$ precipitation to a $NaUO_2Ac_3$ process. Because of the rapid falling off in decontamination factors with each succeeding $NaUO_2Ac_3$ precipitate, however, this process is not attractive.

Adsorption (IR-1) - Lanthanum Fluoride

A preliminary test of coupling adsorption extraction method No. 1 to a modified LaF_3 cycle with a by-product and product precipitation gave an overall yield of 75% and a gamma decontamination factor of 250. This coupling seems to be of minor importance.

Adsorption (IR-1) - Lanthanum Hydroxide-Columbic Oxide-Sodium Uranyl Acetate

Adsorption extraction method No. 1 can be coupled to the $NaUO_2Ac_3$ process through intermediate precipitations of $La(OH)_3$ and Cb_2O_5. In a direct coupling to the $NaUO_2Ac_3$ process, the high sulfate ion concentration in the product solution in adsorption extraction method No. 1 precludes the use of $K_2Cr_2O_7$ as an oxidizing agent in the first $NaUO_2Ac_3$ cycle and also makes necessary a high acetate concentration for complete precipitation of $NaUO_2Ac_3$. To overcome the above difficulties, a $La(OH)_3$ cross-over can be made to eliminate the sulfate. This $La(OH)_3$ product precipitate can be dissolved in HNO_3, and then Cb_2O_5 by-product and $NaUO_2Ac_3$ product precipitations are made (CN-1233).

Adsorption (IR-1) - Adsorption (IR-1)

Adsorption (IR-1) extraction method No. 1 can also be coupled to a second adsorption (IR-1) step. In this process the Pu solution from the first column is neutralized to pH 2.6 and adjusted to 1.25 M sulfate ion and passed through a second column of Amberlite IR-1. This two-stage method is of little value because the decontamination in the second column is specific for only a few cations and the overall decontamination is small. Whereas a large amount of hard gamma is retained in the first column, apparently none is retained in the second column.

Adsorption (IR-1) - Ferron - Adsorption (IR-1)

Another coupling of two Amberlite IR-1 adsorption columns involves intermediate complexing with ferron (7-iodo-8-hydroxyquinoline-5 sulfonic acid). In this coupling the $NaHSO_4$ product solution from the IR-1 column, adsorption extraction method No. 1, is diluted about 5-fold, brought to a pH 5-6, complexed with ferron, and passed through the second IR-1 column. This latter column does not adsorb the complexed Pu but adsorbs the rare earth fission products almost completely. In laboratory tests, 95-98% Pu and only about 1% rare earth and alkaline earth fission products passed through the column. The adsorbed fission products were elutriated completely with 1.25 M $NaHSO_4$. Experiments at high levels need to be performed to determine the exact decontamination obtainable in the second column.

Adsorption (IR-1) - Adsorption (IR-4)

Adsorption (IR-1) extraction method No. 2 can be coupled to an adsorption step using Amberlite IR-4 resin. In this coupling the $H_2C_2O_4$ product solution from the column of IR-1 is passed through another column containing IR-4, and then the adsorbed Pu is elutriated with 4 N H_2SO_4. This second adsorption step is promising as a method of removing the Pu from the $H_2C_2O_4$ solution for subsequent coupling to a precipitation process. The decontamination effected by this step is less than 5, so additional processing is required. This coupling would not make possible an all-adsorption process because of the low decontamination obtained.

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Adsorption (IR-1) - Titanium Zeolite

Adsorption (IR-1) extraction method No. 3 can be coupled to a titanium zeolite adsorption step. In cooperation with the Research Products Corp. a titanium zeolite adsorbent has been developed by the Metallurgical Laboratory. This so-called titanium zeolite exhibited a highly selective adsorption capacity for Pu and practically none for beta. It does not decontaminate Cb and Zr. Therefore, they must be removed by the first column (IR-1). Extensive investigations have established that the best titanium zeolite is made by briquetting a 95% Sherwin-Williams titanium and 5% Aratone mica at about 15,000 p.s.i. and calcining at 1000°C. for 45 minutes. This zeolite is physically stable but has a low transfer rate.

The titanium zeolite in this coupling is used as the decontamination agent following adsorption extraction method No. 3, in which a high decontamination of Zr and Cb is obtained by the use of a H_3PO_4 by-product wash. The coupling is carried out by neutralizing the $NaHSO_4$ product solution from the Amberlite IR-1 column to a pH of 3.5 and passing the neutralized solution through the titanium zeolite bed. Less than 1% of the fission products are adsorbed by the zeolite and of these 95% are preferentially desorbed by a 0.05 N HNO_3 wash. The Pu is then elutriated with a $NaHSO_4$ solution of the same composition as the original Amberlite IR-1 elutriant. This solution can again be neutralized to a pH of 3.5 and a second decontamination cycle carried out. Overall decontamination factors of 5×10^3 have been obtained for an extraction and one decontamination cycle. This process, while extremely promising has not yet been advanced to the design stage. In addition, the limited number of column runs made to date have been complicated in some cases by low Pu yields as a result of the precipitation of impurities in the reagents used.

Adsorption (IR-1) - Chloroform Extraction

Adsorption (IR-1) extraction method No. 2 can be coupled to a $CHCl_3$ extraction process. In this coupling the $H_2C_2O_4$ product solution is adjusted to pH 8 by adding NH_4OH. Cupferron (ammonium-nitrosophenylhydroxylamine) is then added to complex the Pu. This solution is passed countercurrently through a column where the Pu is extracted by $CHCl_3$. The $CHCl_3$ solution is next passed through another column where the Pu is extracted by 0.04 M $H_2C_2O_4$. In laboratory tests the following results were obtained.

TABLE IX

Laboratory Test Results on Adsorption (IR-1) - Chloroform Extraction Process

Step		Volume Reduction based on 10% UNH	Yield % Pu	Overall Decontamination β	Overall Decontamination γ
Column extraction with IR-1		4	96	10^2	10^2
Batch extraction with $CHCl_3$	one decontamination cycle	10	93	$>10^4$	$>10^4$
Batch extraction with $H_2C_2O_4$		20		$>10^5$	10^5
Overall		800	93	$>10^5$	$>10^5$

This process looks promising from the standpoint of high volume reduction and decontamination, but needs further verification.

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TABLE X

LABORATORY TEST RESULTS ON ADSORPTION COUPLING PROCESSES

dsorption xtraction ethod umber	Adsorption Extraction Performance			Coupling Performance												Overall Performance		
				Ppt. #1				Ppt. #2				Ppt. #3						
	β D.F.	γ D.F.	Yield	Type of Ppt.	β D.F.	γ D.F.	Yield	Type of Ppt.	β D.F.	γ D.F.	Yield	Type of Ppt.	β D.F.	γ D.F.	Yield	β D.F.	γ D.F.	Yield
1	1.5	2.2	98	$BiPO_4$-B.P.*	3.3	2.7	-----	$BiPO_4$-P.*	10.6	10.4	91	---- -- ---	---	---	-----	53	62	89
1	1.5	2.2	98	$BiPO_4$-P.	3.0	4.0	-----	$BiPO_4$-B.P.	4.5	4.0	--	$BiPO_4$-P.	36?	25?	91	730	880	89
1	1.5	2.2	98	$NaUO_2Ac_3$-P.	173	108	-----	$NaUO_2Ac_3$-B.P.	3.0	3.0	91	---- -- ---	---	---	-----	780	715	89
1	1.5	2.2	98	$NaUO_2Ac_3$-P.	665	144	-----	$BiPO_4$-B.P.	51	36	51	---- -- ---	---	---	-----	$5.1x10^4$	$1.1x10^4$	50
1	1.5	2.2	98	Ferron complexed. 2nd IR-1 column.												600-6000	600-6000	98
1	1.5	2.2	98	Titanium zeolite	985	136	68									$4x10^3$	$4x10^3$	32
2	100	67	95	$BiPO_4$-P.	1.1	---	-----	$BiPO_4$-B.P.	120	--	92	---- -- ---	---	---	-----	$1.3x10^4$	---	88
2	100	67	95	$U(C_2O_4)_2$				$NaUO_2Ac_3$								$3x10^5$	$3x10^5$	90
2	100	67	95	$U(C_2O_4)_2$-P.	1.3	3.3	**	$NaUO_2Ac_3$-P.	>2350	>1600	75	$BiPO_4$-P.				$>3.1x10^5$	$>3.5x10^5$	71
2	100	67	95	$U(C_2O_4)_2$-P.	1.3	3.3	**	$BiPO_4$-B.P.				$BiPO_4$-P.				$>10^3$	$>10^3$	90
2	100	67	95	Cupferron complexed. $CHCl_3$ ext.				$H_2C_2O_4$ ext.								$>10^5$	$>10^5$	93
2	100	67	95	IR-4		<5											<335	85

* Indicates by-product or product precipitation.

** Product yield in doubt due to analytical difficulties.

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FRACTIONAL VOLATILIZATION PROCESS

The only fractional volatilization process which has been investigated is the dry fluoride process.

Dry Fluoride

In the so-called dry fluoride process, F_2 is passed over the U slugs and volatile fluorides of U, Pu and a few fission products are formed. Most of the fission products are left as residues. The volatile fluorides are condensed and then separated in a distillation column.

Status: The status of the dry fluoride process as of June 1, 1944 is as follows. This process has not been developed sufficiently for plant design and operation. Semi-works fluorination runs have been made successfully, but an overall process including complete extraction, decontamination and isolation steps has not been tested either in the laboratory or the semi-works. Although the dry fluoride extraction step probably could be coupled to a wet precipitation process, such a coupling apparently has not been tested. There are no data available on decontamination and yields for a complete process involving fluorination. Not only is considerable experimental work yet required to perfect such a process, but the entire equipment design must be developed and tested, with the exception of the reactor for which a preliminary design is given in report CN-1206. It should be emphasized that this dry process is only in the very initial state of development and appears to present several operational difficulties such as temperature control and maintenance due to severe corrosion.

Jacket Removal: The Al jackets can be removed by the same solution method as used in the wet processes and described in a previous section of this report, "Jacket Removal". However, this procedure would necessitate the use of a special dissolver designed to permit the complete insertion of a basket containing the slugs for the jacket dissolving step and the subsequent removal of this basket with the bare slugs for transfer to the dry fluoride extraction equipment. In the wet processes, the slugs are dumped from the basket into the dissolver and completely dissolved therein. An alternate method of jacket removal is to lacerate the jackets before charging into the reactor; however, this procedure presents the difficulty of later removing from the reactor these jackets, which will have fission activity deposited on them. It might be possible to discharge them out the top by revolving the reactor or through a trap door in the bottom or side. The mechanical problems involved here, however, have not been investigated.

Fluorination: The dry fluoride process described in the previous survey report CN-1603 had a three-step fluorination procedure. The following equations represent the successive reactions which occurred in the reactor by passing through the gases shown. These equations are revisions based on more recent tests.

$$2\,U + 3\,H_2 \xrightarrow{250^\circ C.} 2\,UH_3$$

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$$2\,UH_3 + 8\,HF \xrightarrow{400^\circ C.} 2\,UF_4 + 7\,H_2$$

$$UF_4 + F_2 \xrightarrow{500^\circ C.} UF_6 \text{ (and } PuF_6)$$

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[redacted] [redacted] [redacted]

Further fluorination tests on a semi-works scale have shown that caking of UF_4 occurs in the second step and the reaction does not go to completion. The use of temperatures as high as 700°C. for this reaction gave no improvement. Mechanical agitation and vibration to prevent this caking were considered, but no study of these methods was made owing to the difficulties in application to plant design and also because the following two-step procedure appeared at that time.

The two-step fluorination method consisted of performing the first two reactions simultaneously and then following with the regular third reaction. In this method the metal was converted to the hydride (UH_3) by a hydrogen atmosphere in the upper part of the reactor. This hydride then fell through a supporting grating for the slug into an atmosphere of HF and was converted to UF_4. Undue mixing of the two gases was prevented by introducing H_2 at the top and HF at the bottom of the reactor, and removing both gases through an exit near the middle. The presence of moderate concentrations of HF in the H_2 reaction had little more effect than that caused by lowering the H_2 partial pressure. Uranium tetrafluoride (UF_4) did not form on the slug and prevent further hydrogenation. This two-step method not only eliminated the caking problem, but also decreased the time for the first two reactions nearly to that previously required for hydrogenation alone; however, further work was discontinued in favor of the following one-step method.

The one-step method consists of a direct fluorination of the metal under a F_2 pressure of 40 lb./sq.in. Although only a few semi-works runs have been made in this manner, this process appears to be the most promising. The following proposed dry fluoride separation process is based on the one-step fluorination procedure.

Extraction and Decontamination: The dry fluoride process as visualized at present consists of a fluorination and subsequent fractional distillation to accomplish extraction from U and also partial decontamination. Although the fluorination step may be fairly well established, the distillation step apparently has not been tested, and may be difficult. Further decontamination and isolation by dry or wet methods would be required. Decontamination by coupling to a wet separation process could probably be accomplished without too much difficulty. The dry decontamination system appears feasible but would need to be proved.

The proposed fluorination procedure (one-step) can be best described by reference to the attached flowsheet, Figure 5. This flowsheet as well as other principal details of the dry fluoride process outlined here were taken from report CN-1206. The reactor consists essentially of a shallow round tank with a removable liner and cover. The liner can be discarded whenever sufficient fission activity collects on it. The bottom of the reactor forms the top of a baffled heat exchange chamber, which heats or cools the reactor as required by means of air from a blower-furnace system outside the cell. The slugs are placed flat against the bottom of the reactor for good heat transfer. After the cover has been bolted on, F_2 is introduced and the pressure is maintained at 40 lb./sq.in. by opening slightly the valve to the stack. The F_2 is obtained from a series of electrolytic cells located near the reactor. The reactor is heated sufficiently to start fluorination of the metal. Since this is an exothermic reaction, the vessel is cooled to maintain a reaction temperature of around 500°C. at the metal surface. Controlling the fluorination temperature may be difficult. The

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resulting UF_6 vapor, sweeping fluorides of Pu and volatile fission products with it, passes through a heated pipe to the boiler of a distillation unit where it is condensed as a liquid solution under a pressure of 40 lb./sq.in. and a temperature around 75°C. The use of pressure in the system permits condensation of UF_6 as a liquid rather than as a solid. The non-condensible gases, including Kr and Xe, pass out the stack. About 75% of the fission products are probably non-volatile and remain in the reactor.

After the fluorination reaction is complete, the distillation system is operated under pressure at total reflux until the concentration of low-boiling fission products, Mo and Te, etc. in the top of the column reaches a constant value. The condensate is then drained to by-product storage. This batch distillation and draw-off procedure is repeated until the charge in the column is sufficiently free of low-boiling fission products. Next the column is operated at a fairly low reflux ratio and the UF_6 is drawn off continuously from the reflux hold-up tank and drained to storage. Upon cooling to room temperature the UF_6 forms a solid. The residues in the still presumably contain Pu and the high-boiling fission products, such as Cb and Zr, dissolved in about one gallon of UF_6. The control of pressure and temperature on the distillation column might be difficult. During this distillation the reactor is kept hot to prevent any liquid from condensing therein. Probably a small amount of gas (F_2 or N_2) would be bled in to keep out vapors that might enter from the column.

Further decontamination is accomplished by dry or wet methods. In the dry method the UF_6 is all vaporized off, condensed, and drained to storage. Then HF at 500°C. is passed over the solid residue to volatilize Cb and Zr by-products. This should leave a sufficiently decontaminated Pu as residue. In the wet method the 1-gal. solution of UF_6 plus Pu and some fission products is steam jetted from the boiler into a precipitator tank containing H_2O. The steam converts the volatile fluorides into non-volatile, water-soluble forms. Regular wet process decontamination is then carried out.

Waste Disposal: If the Al jackets are dissolved off the slugs, their waste solution would be neutralized with NaOH, and stored in buried concrete storage tanks with air-cooled condensers. If the jackets are lacerated, they probably would be discharged from the reactor into a buried tank.

As mentioned previously, probably 75% of the fission activity would be non-volatile and remain in the reactor. If a removable liner is used, this could be replaced periodically. However, it may be desirable to design all the dry fluoride equipment as a compact unit to be installed underground and abandoned whenever the fission activity builds up to a point where further operation is undesirable. It is believed to be impractical to clean the equipment.

The UF_6 is to be stored in a separate tank and the U can be recovered if desired. The UF_6 should be relatively free of fission activity. The volatile fission products would be stored in another buried tank. The radioactive gases passing out the stack are diluted to limits tolerable for people in the vicinity as is the practice with such gases from the regular dissolvers for the wet processes.

Corrosion: Operation of the dry fluoride process probably would present severe corrosion problems because of the presence of F_2, UF_6, and possibly HF at high temperatures. Although the equipment would be fabricated from monel metal which has a high resistance to corrosion from these chemicals, it appears that maintenance could be a definite problem. As shown on the flowsheet, the valves would be located in an individual cell to facilitate repair. The use of N_2 counterflows instead of valves might be incorporated in the design. If further development work is done on this process, extensive corrosion tests should be included.

Advantages and Disadvantages: Advantages of the dry fluoride process are:

1. The equipment is relatively simple because no agitators, centrifuges, etc. are required.
2. Only one major chemical is needed (F_2).
3. Waste volumes are small.
4. UF_6 is essentially free of activity and stored in a useful form.

Disadvantages of the process include:

1. Critical temperature and pressure control appears necessary.
2. Severe corrosion problems are likely.
3. A special dissolver is required unless the jackets are lacerated, in which case there is a difficult jacket disposal problem.
4. Disposal of fission activity may be difficult.
5. There is some danger of lines plugging.

Figure 1.

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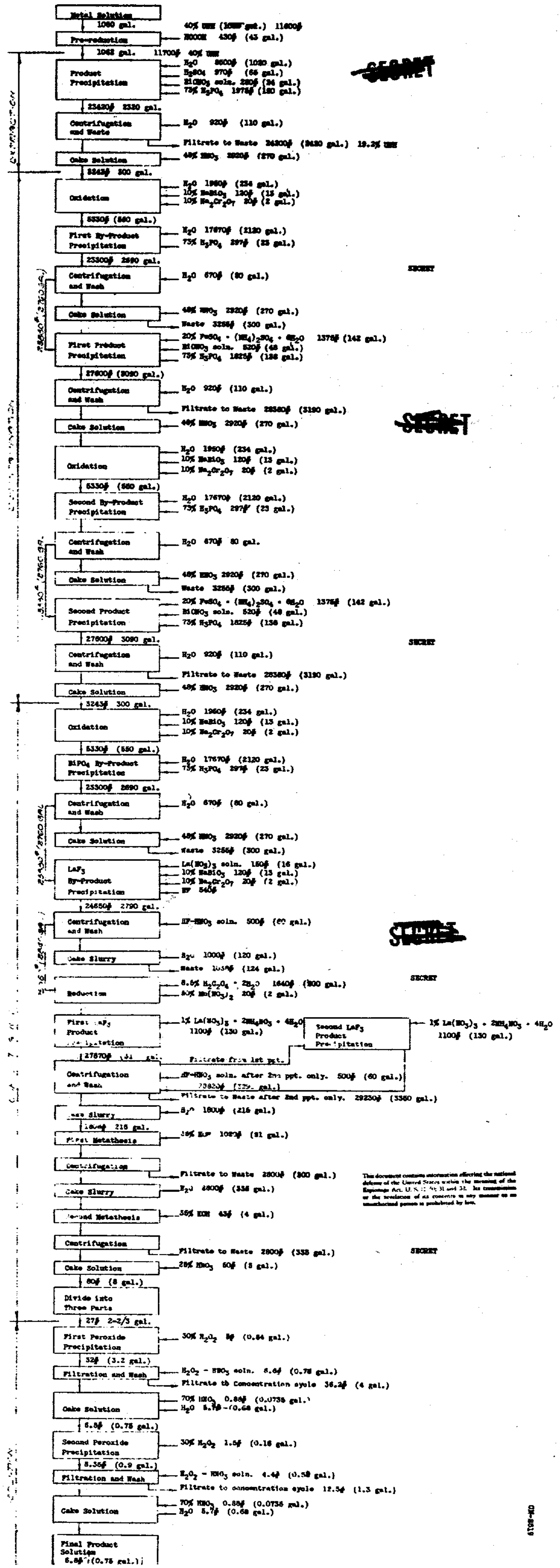
MAIN LINE PROCESS

Condensed from flowsheet March 28, 1944, by J. E. Work

Basis: 2200 lb. metal


Metal Solution
1060 gal.
40% UNH (1060 gal.) 11600#
Pre-reduction
HCOOH 430# (43 gal.)
1062 gal. 11700# 40% UNH
Product Precipitation
H_2O 8600# (1020 gal.)
H_2SO_4 970# (66 gal.)
$BiONO_3$ soln. 280# (24 gal.)
73% H_3PO_4 1975# (180 gal.)
23420# 2330 gal.
Centrifugation and Waste
H_2O 920# (110 gal.)
Filtrate to Waste 24300# (2420 gal.) 19.2% UNH
Cake Solution
48% HNO_3 2920# (270 gal.)
3243# 300 gal.
Oxidation
H_2O 1960# (234 gal.)
10% $NaBiO_3$ 120# (13 gal.)
10% $Na_2Cr_2O_7$ 20# (2 gal.)
5330# (560 gal.)
First By-Product Precipitation
H_2O 17670# (2120 gal.)
73% H_3PO_4 297# (23 gal.)
25300# 2890 gal.
Centrifugation and Wash
H_2O 670# (80 gal.)
Cake Solution
48% HNO_3 2920# (270 gal.)
Waste 3255# (300 gal.)
First Product Precipitation
20% $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ 1378# (142 gal.)
$BiONO_3$ soln. 520# (48 gal.)
73% H_3PO_4 1825# (138 gal.)
27600# (3090 gal.)
Centrifugation and Wash
H_2O 920# (110 gal.)
Filtrate to Waste 28380# (3190 gal.)
Cake Solution
48% HNO_3 2920# (270 gal.)
Oxidation
H_2O 1960# (234 gal.)
10% $NaBiO_3$ 120# (13 gal.)
10% $Na_2Cr_2O_7$ 20# (2 gal.)
5330# (560 gal.)
Second By-Product Precipitation
H_2O 17670# (2120 gal.)
73% H_3PO_4 297# (23 gal.)
Centrifugation and Wash
H_2O 670# 80 gal.
Cake Solution
48% HNO_3 2920# (270 gal.)
Waste 3255# (300 gal.)
Second Product Precipitation
20% $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ 1378# (142 gal.)
$BiONO_3$ soln. 520# (48 gal.)
73% H_3PO_4 1825# (138 gal.)
27600# 3090 gal.
Centrifugation and Wash
H_2O 920# (110 gal.)
Filtrate to Waste 28380# (3190 gal.)
Cake Solution
48% HNO_3 2920# (270 gal.)
3243# 300 gal.
Oxidation
H_2O 1960# (234 gal.)
10% $NaBiO_3$ 120# (13 gal.)
10% $Na_2Cr_2O_7$ 20# (2 gal.)
5330# (550 gal.)
$BiPO_4$ By-Product Precipitation
H_2O 17670# (2120 gal.)
73% H_3PO_4 297# (23 gal.)
25300# 2890 gal.
Centrifugation and Wash
H_2O 670# (80 gal.)
Cake Solution
48% HNO_3 2920# (270 gal.)
Waste 3255# (300 gal.)
LaF_3 By-Product Precipitation
$La(NO_3)_3$ soln. 150# (16 gal.)
10% $NaBiO_3$ 120# (13 gal.)
10% $Na_2Cr_2O_7$ 20# (2 gal.)
HF 540#
24650# 2790 gal.
Centrifugation and Wash
$HF-HNO_3$ soln. 500# (60 gal.)
Cake Slurry
H_2O 1000# (120 gal.)
Waste 1058# (124 gal.)
Reduction
8.6% $H_2C_2O_4 \cdot 2H_2O$ 1640# (200 gal.)
50% $Mn(NO_3)_2$ 20# (2 gal.)
First LaF_3 Product Precipitation
1% $La(NO_3)_3 \cdot 2NH_4NO_3 \cdot 4H_2O$ 1100# (130 gal.)
Second LaF_3 Product Precipitation
1% $La(NO_3)_3 \cdot 2NH_4NO_3 \cdot 4H_2O$ 1100# (130 gal.)
27870#
Filtrate from 1st ppt.
Centrifugation and Wash
$HF-HNO_3$ soln. after 2nd ppt. only. 500# (60 gal.)
Filtrate to Waste after 2nd ppt. only. 29230# (3360 gal.)
Cake Slurry
H_2O 1800# (216 gal.)
216 gal.
First Metathesis
50% KF 1020# (91 gal.)
Centrifugation
Filtrate to Waste 2800# (300 gal.)
Cake Slurry
H_2O 2800# (336 gal.)
Second Metathesis
50% KOH 43# (4 gal.)
Centrifugation
Filtrate to Waste 2800# (335 gal.)
Cake Solution
28% HNO_3 60# (8 gal.)
80# (8 gal.)
Divide into Three Parts
27# 2-2/3 gal.
First Peroxide Precipitation
30% H_2O_2 8# (0.84 gal.)
32# (3.2 gal.)
Filtration and Wash
$H_2O_2-HNO_3$ soln. 8.6# (0.78 gal.)
Filtrate to Concentration cycle 36.2# (4 gal.)
Cake Solution
70% HNO_3 0.88# (0.0735 gal.)
H_2O 5.7# (0.68 gal.)
6.5# (0.75 gal.)
Second Peroxide Precipitation
30% H_2O_2 1.5# (0.16 gal.)
8.35# (0.9 gal.)
Filtration and Wash
$H_2O_2-HNO_3$ soln. 4.4# (0.53 gal.)
Filtrate to concentration cycle 12.5# (1.3 gal.)
Cake Solution
70% HNO_3 0.88# (0.0735 gal.)
H_2O 5.7# (0.68 gal.)
Final Product Solution
6.5# (0.75 gal.)
EXTRACTION

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CN-2519
Figure 2.

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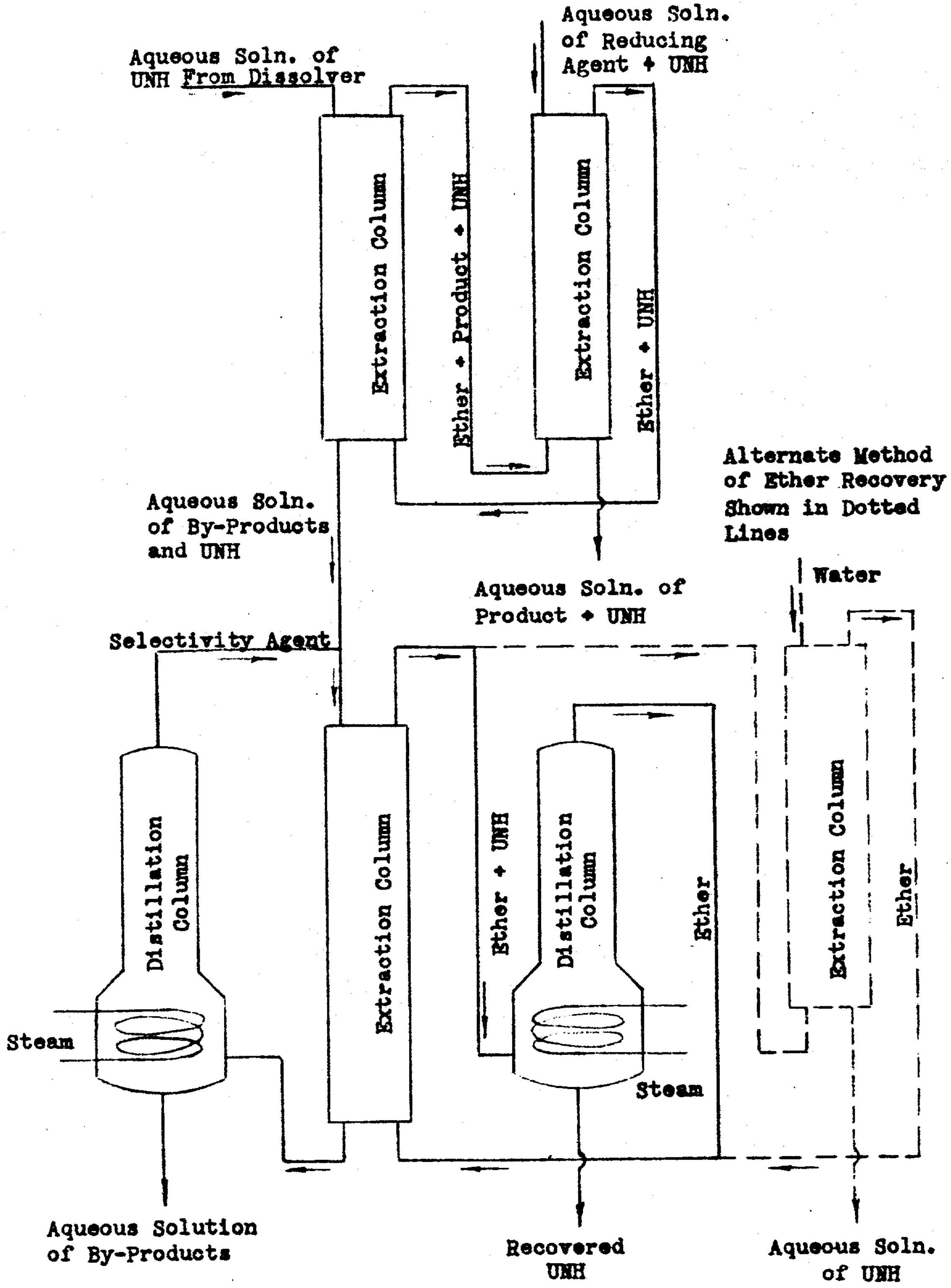
ETHER EXTRACTION PROCESS

Proposed Scheme for Separation of Product and Recovery of Uranium

June 1, 1944


Aqueous Soln. of UNH From Dissolver
Aqueous Soln. of Reducing Agent + UNH
Extraction Column
Ether + Product + UNH
Extraction Column
Ether + UNH
Alternate Method of Ether Recovery Shown in Dotted Lines
Aqueous Soln. of By-Products and UNH
Aqueous Soln. of Product + UNH
Water
Selectivity Agent
Distillation Column
Extraction Column
Ether + UNH
Distillation Column
Ether
Extraction Column
Ether
Steam
Steam
Aqueous Solution of By-Products
Recovered UNH
Aqueous Soln. of UNH

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ADSORPTION EXTRACTION METHOD NO. 1

Basis: 2200 lbs. Metal

Reference: CN-1431
June 1, 1944

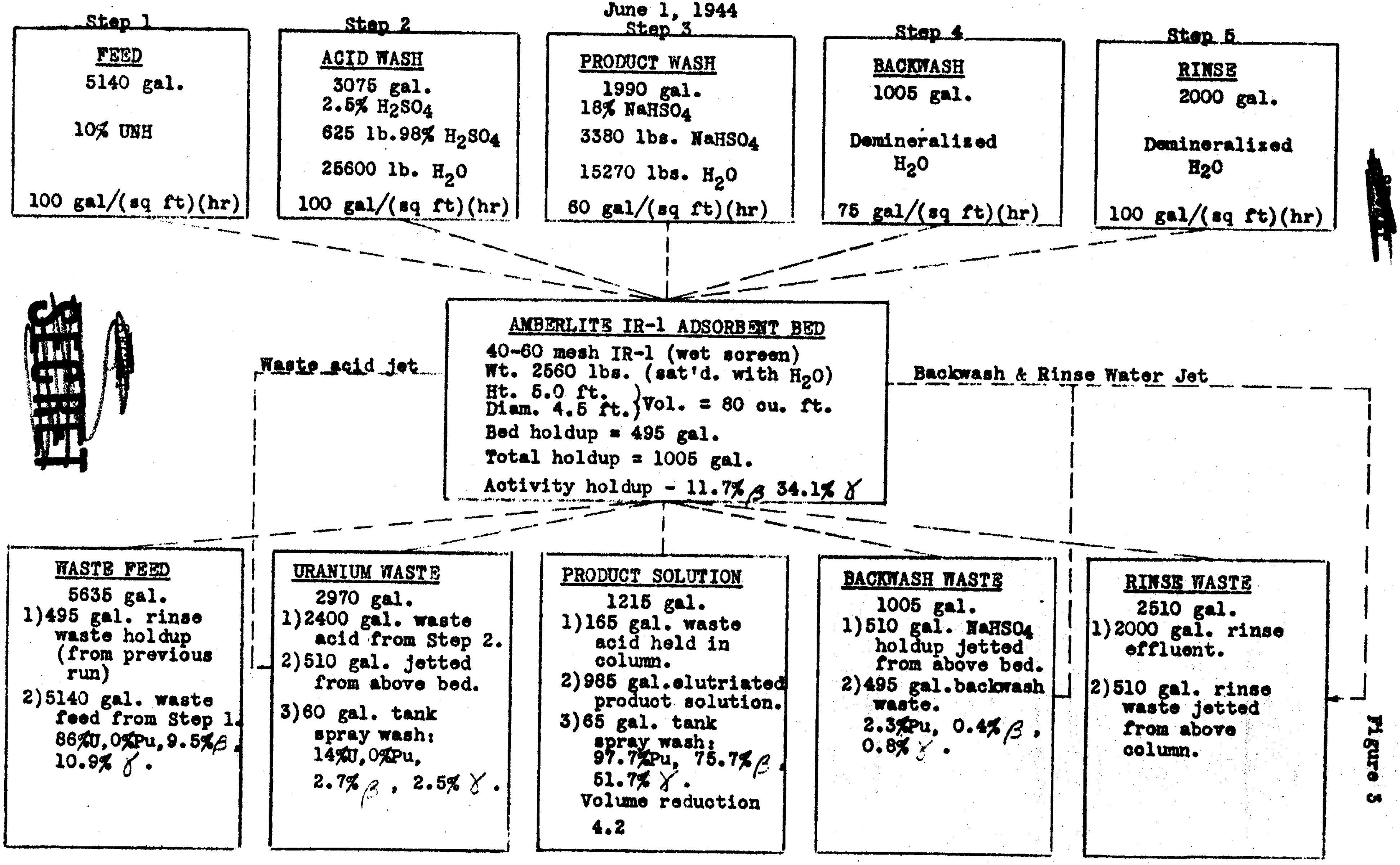
Step 1
FEED
5140 gal.
10% UNH
100 gal/(sq ft)(hr)
Step 2
ACID WASH
3075 gal.
2.5% H2SO4
625 lb. 98% H2SO4
25600 lb. H2O
100 gal/(sq ft)(hr)
Step 3
PRODUCT WASH
1990 gal.
18% NaHSO4
3380 lbs. NaHSO4
15270 lbs. H2O
60 gal/(sq ft)(hr)
Step 4
BACKWASH
1005 gal.
Demineralized H2O
75 gal/(sq ft)(hr)
Step 5
RINSE
2000 gal.
Demineralized H2O
100 gal/(sq ft)(hr)
AMBERLITE IR-1 ADSORBENT BED
40-60 mesh IR-1 (wet screen)
Wt. 2560 lbs. (sat'd. with H2O)
Ht. 5.0 ft.
Diam. 4.5 ft.
Vol. = 80 cu. ft.
Bed holdup = 495 gal.
Total holdup = 1005 gal.
Activity holdup - 11.7% β 34.1% γ
Waste acid jet
Backwash & Rinse Water Jet
WASTE FEED
5635 gal.
1)495 gal. rinse waste holdup (from previous run)
2)5140 gal. waste feed from Step 1. 86%U, 0%Pu, 9.5%β, 10.9% γ.
URANIUM WASTE
2970 gal.
1)2400 gal. waste acid from Step 2.
2)510 gal. jetted from above bed.
3)60 gal. tank spray wash: 14%U, 0%Pu, 2.7%β, 2.5% γ.
PRODUCT SOLUTION
1215 gal.
1)165 gal. waste acid held in column.
2)985 gal. elutriated product solution.
3)65 gal. tank spray wash: 97.7%Pu, 75.7%β, 51.7% γ.
Volume reduction 4.2
BACKWASH WASTE
1005 gal.
1)510 gal. NaHSO4 holdup jetted from above bed.
2)495 gal. backwash waste.
2.3%Pu, 0.4%β, 0.8% γ.
RINSE WASTE
2510 gal.
1)2000 gal. rinse effluent.
2)510 gal. rinse waste jetted from above column.

Figure 3

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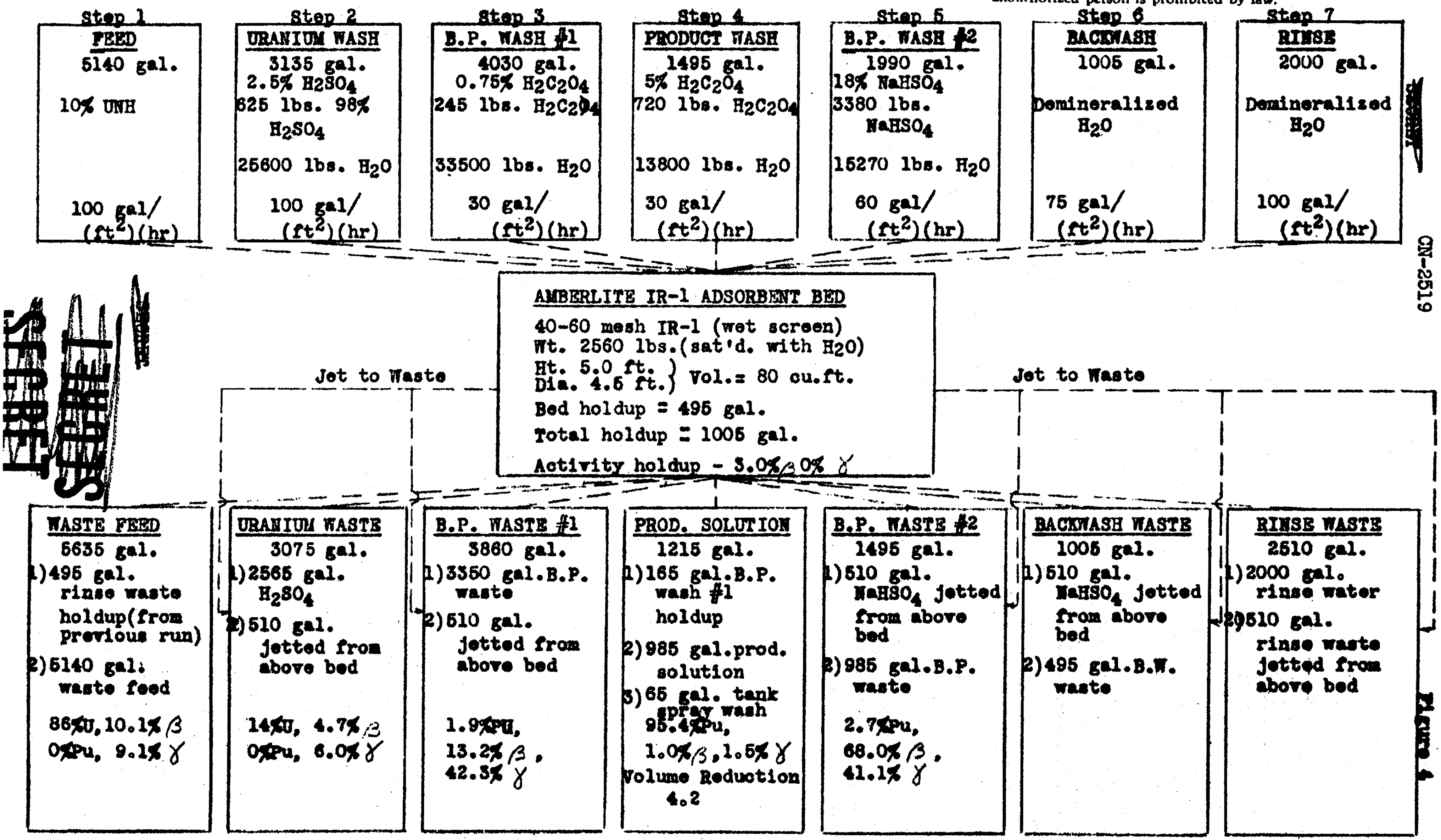
ADSORPTION EXTRACTION METHOD NO. 2.

Basis: 2200 lbs. Metal
Reference: CN-1431
June 1, 1944



Step 1
FEED
5140 gal.
10% UNH
100 gal/ $(ft^2)(hr)$

Step 2
URANIUM WASH
3135 gal.
2.5% H_2SO_4
625 lbs. 98% H_2SO_4
25600 lbs. H_2O
100 gal/ $(ft^2)(hr)$

Step 3
B.P. WASH #1
4030 gal.
0.75% $H_2C_2O_4$
245 lbs. $H_2C_2O_4$
33500 lbs. H_2O
30 gal/ $(ft^2)(hr)$

Step 4
PRODUCT WASH
1495 gal.
5% $H_2C_2O_4$
720 lbs. $H_2C_2O_4$
13800 lbs. H_2O
30 gal/ $(ft^2)(hr)$

Step 5
B.P. WASH #2
1990 gal.
18% $NaHSO_4$
3380 lbs. $NaHSO_4$
15270 lbs. H_2O
60 gal/ $(ft^2)(hr)$

Step 6
BACKWASH
1005 gal.
Demineralized H_2O
75 gal/ $(ft^2)(hr)$

Step 7
RINSE
2000 gal.
Demineralized H_2O
100 gal/ $(ft^2)(hr)$

AMBERLITE IR-1 ADSORBENT BED
40-60 mesh IR-1 (wet screen)
Wt. 2560 lbs.(sat'd. with H_2O)
Ht. 5.0 ft. } Vol.= 80 cu.ft.
Dia. 4.5 ft. }
Bed holdup = 495 gal.
Total holdup = 1005 gal.
Activity holdup - 3.0% β 0% γ

Jet to Waste

Jet to Waste

WASTE FEED
5635 gal.
1) 495 gal. rinse waste holdup (from previous run)
2) 5140 gal. waste feed
86% U, 10.1% β
0% Pu, 9.1% γ

URANIUM WASTE
3075 gal.
1) 2565 gal. H_2SO_4
2) 510 gal. jetted from above bed
14% U, 4.7% β
0% Pu, 6.0% γ

B.P. WASTE #1
3860 gal.
1) 3350 gal. B.P. waste
2) 510 gal. jetted from above bed
1.9% Pu,
13.2% β,
42.3% γ

PROD. SOLUTION
1215 gal.
1) 165 gal. B.P. wash #1 holdup
2) 985 gal. prod. solution
3) 65 gal. tank spray wash
95.4% Pu,
1.0% β, 1.5% γ
Volume Reduction 4.2

B.P. WASTE #2
1495 gal.
1) 510 gal. $NaHSO_4$ jetted from above bed
2) 985 gal. B.P. waste
2.7% Pu,
68.0% β,
41.1% γ

BACKWASH WASTE
1005 gal.
1) 510 gal. $NaHSO_4$ jetted from above bed
2) 495 gal. B.W. waste

RINSE WASTE
2510 gal.
1) 2000 gal. rinse water
2) 510 gal. rinse waste jetted from above bed

Figure 4

Figure 5.

[redacted]

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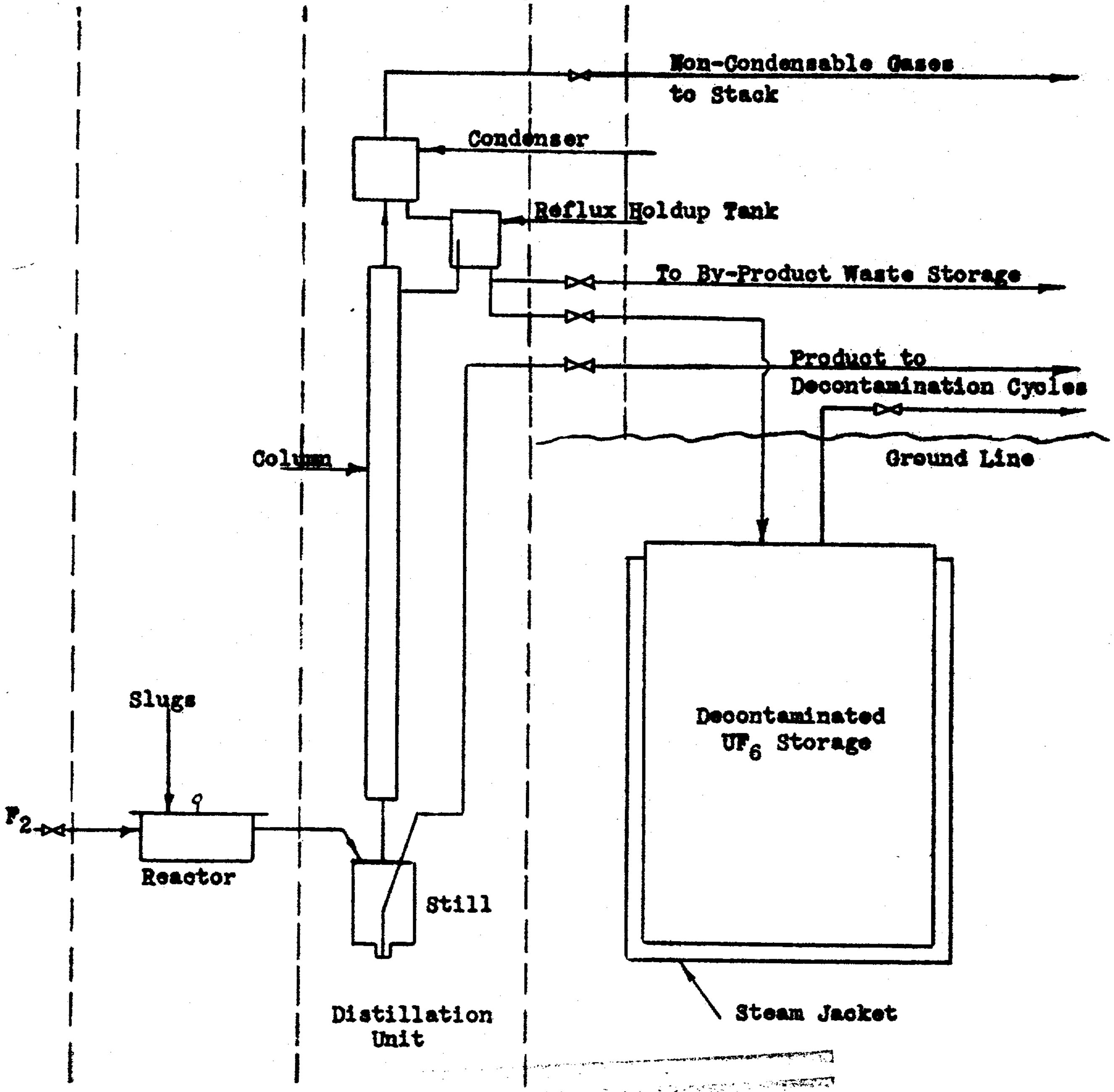
[redacted] PROCESS
One Step Fluorination
(From CN-1206)

June 1, 1944


Non-Condensable Gases to Stack
Condenser
Reflux Holdup Tank
To By-Product Waste Storage
Product to Decontamination Cycles
Ground Line
Column
Decontaminated UF_6 Storage
Slugs
F_2
Reactor
Still
Distillation Unit
Steam Jacket

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